MORPHOLOGICAL, CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF SOME INDIAN FLY ASHES

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by

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CERTIFICATE

This is to certify that the thesis entitled, *"Morphological, Chemical, and Mineralogical Characterization of some Indian Fly Ashes* ", by Sarat Kumar Das is a record of work carried out by him under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

The present study concerns with the characterization of some Indian fly ashes in terms of morphology, chemistry and mineralogy. Scanning Electron Microscope(SEM), Energy Dispersive X-Ray(EDX) and X-Ray Diffraction(XRD) techniques found to be suitable tools for these types of studies. The distinction between high and low calcium fly ash has been presented. The variability in the fly ash particularly particle chemistry has been stressed.

In case of low calcium fly ashes the chemistry and mineralogy is shown to be independent of the particle size. In case of high calcium fly ashes the >75μm fractions is shown to be comprised of inert crystalline minerals and the fraction <45μm contains the most reactive minerals and glass.

The quantitative relationships between glass quality and quantity with chemical composition have been shown. The distinct differences between self hardening and pozzolanic reactive potential have been emphasized.

It is stressed that a detailed characterisation of the material along the lines pursued in this study, is a must, before taking decisions regarding effective and economic utilisation of a fly ash.

ACKNOWLEDGEMENT

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Sarat Kumar Das

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CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

In India, thermal power plants supply the major portion of electric power required for the industrial development and rail transport. Unfortunately along with this power supply thermal plants, just like side effects of a medicine, produce vast quantities of waste 90% of which is fly ash. Fly ash affects the environment polluting soil, water and air. This has detrimental effect on human health and the quality of life in the surrounding area. The over land disposal into ash ponds is responsible for leaching heavy metals from fly ash into ground water and possible transmission of trace metals into food chain, though as a whole fly ash is not included in the hazardous waste group. In addition vast areas of land used for dumping fly ash would produce vast tracts of waste land. Properly handled fly ash can be effectively used in many ways, for example:

(1) As light weight aggregate and building blocks

(2) As substitute for cement. With lime or cement it has been used as precast concrete units, sintered cellular concrete etc.

(3) As raw material in cement industry.

(4) As an effective grouting material with cement due to its spherical shape of particles.

(5) Used for soil stabilization of Railway/road embankment, road

bases or for manufacturing clay-fly ash bricks.

(6) As fly ash columns in place of lime columns, and for improvement of soft and weak foundation soils.

(7) Used as embankment material and as reclamation fill for waste land and abandoned mines.

(8) Due to high permeability it has been used to dry out wet soil.

Pozzolanic characteristics of fly ash are strongly controlled by morphology, mineralogy, chemistry and grannulometry which are in turn affected by the quality of coal used and its preprocessing, furnace temperature, efficiency of electric precipitators,and method of disposal and storage(wet or dry) etc.

Ash in the thermal power plant results from the burning of pulverized coal in the range of 1300 -1450^{0} C in the furnace of boiler in presence of nearly 20% excess air. The end product of coal combustion on cooling is rich in spherical particles. These small particles moving upward with high velocity are collected with precipitators to avoid their escape into the atmosphere from the chimneys.This material so collected is called fly ash. Some of the particles get agglomerated to a size large enough to settle down under the influence of gravity.The ashes so collected are called Bottom ash.Fly ash in India is usually mixed with water and is pumped as slurry into the ash pond. Ponded fly ash is known to have inferior pozzolanic properties as compared to that stored in silos.

The chief chemical constituents of fly ash are Silica(SiO_2), Alumina(Al_2O_3), Lime(CaO) and Iron(Fe_2O_3) with traces of SO_3, K_2O andNa_2O. Though there is a wide variation in the chemical contents of fly ash, broadly it can be divided into two groups; high calcium

and low calcium fly ash resulting from burning of sub-bituminous and hard coals respectively. The residual carbon expressed as LOI at $900^{\circ}C$ is high for low calcium fly ash where as high calcium fly ash collected from modern plants hardly has any residual carbon.

The minerals found in low calcium fly ash are quartz,mullite,hematite and magnetite along with alumino-silicate glass, where as high calcium fly ash contains minerals like C_3A, CS ,$C\bar{S}$ and calcium aluminate glass both of which are highly reactive and impart cementing effect. The crystalline minerals present in low calcium fly ash are inert and do not exhibit pozzolanic reactivity.

The quantity of glass and alkali percentage depend upon the temperature of furnace.The temperature of $1500-1700^{\circ}$ C has found to produce a good pozzolanic fly ash depending on the amount of CaO, K_2O and fineness.

1.2 LITERATURE REVIEW

In this study main emphasis is on the investigation of morphological, chemical and mineralogical characteristics of some of the Indian fly ashes. With a view to compare the results of this study with those reported in literature, a review of the published work is undertaken specifically with respect to methods and tools of investigation adopted by other investigators for such studies. Also some of the methods suggested for classification of fly ashes and the factors governing their pozzolanic characteristics are reviewed.

1.2.1 Morphological characterization

The morphology of fly ash has been studied by both optical and scanning microscope. The fly ash particles are mostly spherical with size range from 1 μm to 100 μm. The oversize particles are mostly

irregular in outline(Mehta;1985).

Watt and Throne (1965) conducted microscopic examination with the help of light optical microscope on various low calcium fly ashes and according to shape, color, texture and crystallinity they have identified various morphological forms(Table-1). Fisher Natusch(1979) with help of light microscopy have found out 11 major morphological classes according to particle shape and degree of opacity. They have given morphogenesis scheme relating 11 morphological classes (Table-2) to the extent and duration of exposure to combustion zone temperature and probable matrix combustion The relative abundance of all particle classes are size dependant. Amorphous and vesicular particles predominates in the coarsest fraction where as solid non-opaque particles predominate in the finest fraction.(Fisher and Natusch;1979).But later the investigation of a high calcium fly ash with help of optical microscope, Koo(1991) found that particles <75 μm show predominantly glassy spherules.

Use of Scanning Electron Microscope(SEM) removes the hurdles in identifying tiny particles and most important contribution of SEM is in study of surface characteristics of particles. Due to the presence of alkali sulphate and some free lime, the high calcium fly ash shows a surface deposit over it unlike low calcium fly ash whose surface is smooth.(Fisher and Natusch;1979).

The study of surface characteristics of low calcium fly ash (Fischer and Natusch;1979) showed five surface morphological characteristics:

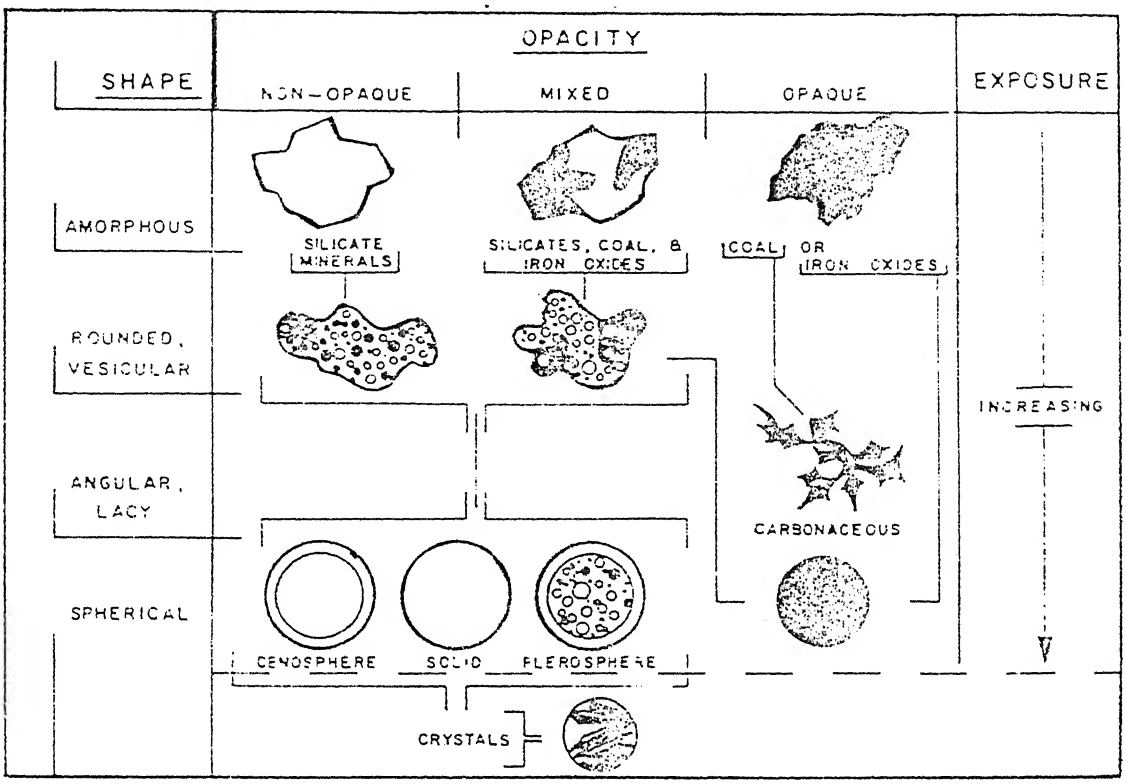
(1)Cenospheres and Plerospheres

(2)Sphere with smooth surface

Table 1 Types of Fly Ash Particles Characterized by Microscopic Examination (Watt & Throne, 1965)

TYPE	Shape	Color	Crystallity and Texture	Size Range μm	Comments
1.	Spherical & rounded	Colorless	a) glassy, clear solid b) glassy, containing small bubbles c) glassy with crystal traces d) predominantly crystalline solid	0–20 10–50	---------
2.	Spherical & rounded	Light brown to Black	Light colored glassy solid	5–30	Deepening color suggest increasing iron content
3.	Rounded	White in reflected light	Light colored glassy solid	10–200	Small and large bubbles giving a range from foam to cenospheres
4.	Irregular	Light brown	Partly crystalline solid	10–100	Irregularity of profile and surface very marked
5.	Irregular	Varicolored in reflected light	-do-	50–500	Agglomerated particles, generally containing red particles and area
6.	Irregular	Black	Solid or porous	20–200	Partially burnt coal particles
7.	Angular	Colorless	Crystalline, solid	10–100	Probably quartz
8.	Angular	Red	-do-	5–50	Probably hematite

Table-2. Particle morphogenesis scheme. for Fly Ashes



(3)sphere with small surface particles

(4)Surface with relatively large droplets.

(5)Iron rich spheres with unusual pattern of coarse surfac

Leonard & Bailey(1982) studied some American fly ashes and found basically four types of morphological features for fly ash particles (1)solid spheres(2)Hollow spheres(cenospheres)(3)clinker like (holey) and irregular and (4)platy particles that are occasionally stacked. The fly ash particles from pulverized coal plants are mostly of spherical shape with some irregular particles whereas fly ash resulting from grate firing plant are not spherical, rather they are rich in grains of undefined form with a porous and fibrous structure.(Möller and Nilson;1985). The study of some low calcium American fly ashes revealed some new features along with some well known features as reported by Diamond(1986). These are summerised as below

(1)Cenospheres and Plerospheres are rather common

(2)Cluster of tiny particles which are bounded either due to thin layer of carbon or fused glass to glass contact

(3)Large platy carbon residue

(4)"Swiss cheese" particles containing small inorganic spherical particles embedded in residual carbon.

(5) A surface deposit over particles

(6) By etching with HF acid two types of internal structures are revealed (a)Characteristic structural lath or needle shape Mullite particles interlocked with each other which has been later reported by Dhir et al.(1988) also and (b)Cubic iron rich ferrite spinel structure.

The Floaters as collected by Float and sink method from fly ashes are also not homogeneous. They exhibit mostly four types of features (1) a minor scum (carbon particles and floater) (2) a major suspended component (spheres <10μm) (3)minor sediments (broken and mis-shapen spheres, clay residues, crystalline materials and some tapped small intact spheres) and (4)Cenospheres which have three zones i.e. inner and outer dominated by glass sandwitching a central zone of mullite crystals.

1.2.2 Chemical characterization

The chemistry of fly ash is governed by the inorganic substances present in the coal. The principal constituents of fly ash are silica(SiO_2), alumina(Al_2O_3), iron oxide(FeO), lime(CaO), magnesia(MgO) sulphate and traces of oxides of potassium and sodium. In addition depending on the coal type and plant operation, fly ashes (specially low calcium) have varying amounts of residual carbon. There is a wide variation of these main constituents of fly ashes as given in Appendix - 1.

The chemical analysis of the fly ash is determined by different procedures like

(1) Chemical Extraction

(2)X-Ray Fluorescence

(3)Atomic Absorption Spectroscopy

(4)Flame Photometry

(5)Energy Dispersive X-Ray (EDX) analysis.

For a complete analysis one needs to use a combination of some of these methods. The method of analysis by chemical extraction has been well standardized (e.g see Sherwood & Ryley;1966). The X-Ray Fluorescence method has been successfully used by calibrating with

ASTM rock standards(VanRoode et al., 1987; Hubbard et al., 1985; Mehta,1986), Where as Koo(1991) has analysed the fly ash using Atomic Absorption Spectroscopy following ASTM E886-88(1989). The K_2O and Na_2O is best analyzed by Flame photometry.

Unlike other pozzolana the fly ash is a highly heterogeneous material. As individual fragments of pulverized coal suspended in hot air, moving rapidly through a brief exposure to high temperature have little possibilities of exchange of mass between separated particles. Since local inorganic compound vary widely, even adjacent particles of similar shape may vary in composition. So overall chemical analysis of fly ash is a statistical matter.(Diamond;1986). It is thus very important to study the composition of individual particles along with an average composition of the whole sample as given by chemical extraction, X-ray fluorescence or atomic absorption methods.

Energy Dispersive X-ray (EDX) is used along with Scanning Electron Microscope(SEM) to determine the composition of individual particles. Fisher and Natusch(1979), Diamond(1986) have used the EDX n characterization of individual fly ash particles. Use of EDX for chemical analysis of stabilized fly ash has been reported by Nontananandh; 1990)

The smooth spheres in low calcium fly ash are mostly rich in Al nd Si where as spheres with small or large droplets over it are omposed of iron core with Al and Si particles over it.The residual arbon is detected from the characteristic Bremstrahlung roduced(Fisher and Natusch;1979).

1.2.3 Mineralogical characterization

Mineralogy of fly ash mostly depends upon the chemical composition of inorganic substance in coal. Powder X-ray diffraction method is one of the important instrument used for mineralogical study of fly ash. There is a distinct difference in mineralogy between high calcium and low calcium fly ash. The minerals that are commonly found in low calcium fly ash are quartz, mullite ($3Al_2O_3.SiO_2$), sillimanite ($Al_2O_3.SiO_2$), hematite(Fe_2O_3) and magnetite(Fe_3O_4). These mineral are not reactive with lime or cement at ordinary temperature.

The high calcium fly ash has minerals like C_3A, CS, CaO and $C\bar{S}$ Which are very reactive and imparts cementing effect. The other minerals found are quartz,hematite and magnetite. It is observed that for Cao content above 15% mullite is generally absent(Yudhbir & Honjo;1991). It may be due to the formation of minerals like C_3A, CS, $C\bar{S}$ and calcium aluminate glass due to high lime content, currently efforts are being made to add limestone in the combustion chamber of pulverized coal or stroker boiler to give a new kind of fly ash(Blondin;1988). The other minerals in some cases have been reported are periclose(MgO) (Mehta;1979) and $Na_3A\bar{S}_6$(Van Roode et al.(1987).

The common clay minerals present in coal are kaolinite, illite and some mixed layer clay minerals.The kaolinite transforms in the solid state to amorphous metakaolinite and mullite, where as the illite clay mineral, due to presence of potash which is a good flushing agent, under goes partial melting and transforms to aluminosilicate glass and some mullite and quartz. (Hubbard et al. ;1985). The carbonates like calcite and dolomite transform to their

oxide and above a certain temperature react with fused clay minerals to form minerals like C_3A etc. Above $1060^{o}C$ CaO absorbs $SO_2$and forms $C\bar{S}$.

The relative proportion of magnetite and hematite depends upon the oxidizing conditions in the furnace as both are derived from pyrite. The roasting of fly ash always increase the proportion of hematite(Simmon & Jeffry; 1960). There may some hematite also present in coal itself(Tsai; 1982). After $1100^{o}C$ some of the hematite transformed to iron spinel like maghematite(γ-Fe_2O_3). In case of high iron fly ash the other form of iron compound may be silicate iron glass, non-magnetic iron($2CaO.Fe_2O_3$) and soluble iron like iron sulphate (Simmon & Jeffry; 1960).

The glass phase in low calcium fly ash is of alumino-silicate type though in cases of high/moderate iron content fly ash, appreciable amount of silicate-iron glass may also be present (Simmon & Jeffry; 1960). The calcium aluminate glass is dominant in cases of high calcium fly ash. The qualitative assessment of glass phase in fly ash can be done from XRD pattern of fly ash (Mehta, 1979; Diamond, 1983). The maximum intensity of diffuse band due to alumino-silicate glass in case of low calcium fly ash is in between 21-25^{o} 2θ where as that for high calcium fly ash it is between 31-35^{o} 2θ (Cu-radiation)(Mehta; 1979).

The peak position of *hump* in the XRD pattern of low calcium fly ash varies linearly between 23-$27^{o}2\theta$ (Cu radiation) with analytical lime content. This shift may be due to structural arrangement in the siliceous glass as CaO content is increased. For high calcium fly ash the position shifts to 32^{o} 2θ due to presence of calcium aluminate type of glass(Diamond; 1983).

There are two methods for quantitative determination of glass phase in fly ash. The quantitative X-ray diffraction method is an indirect method of glass phase determination in which the percentage of crystalline minerals is first determined and then total glass content is given as

glass content = 100 - $\sum$crystalline phase - LOI.

where LOI = loss on ignition (carbon content).

This method has been successfully used by many researchers (Simmon & Jeffry, 1960; Watt& Thorne, 1965; Mehta, 1985; Hubbard et al., 1985; VanRoode et al.., 1987). For low calcium fly ash the glass phase can be directly determined by dissolving fly ash with flourosilicic acid (e.g. see Valent et al. 1988). The glass content of low calcium fly ash varies between 29 to 89% (Yudhbir & Honjo;1991) and that for high calcium this range is 75 to 95 % (Mehta;1985).

For some of the British low calcium fly ash Hubbard et al. (1985) have established a direct relationship between K/A *10 with total glass content. The K/A ration is defined as $K_2O/M.W. \div Al_2O_3/M.W$, where M.W. is the molecular weight.

1.2.4 Factors Controlling Pozzolanic Reactivity

Chemical composition, nature of minerals :- inert or reactive, quality and quantity of glass phase, amount of free lime, residual carbon content, and fineness are some of the important factors that have been shown to control the Pozzolanic reactivity of fly ashes (Yudhbir and Honjo;1991). The fineness is helpful only for early strength development of reaction.

The calcium-aluminate glass in high calcium fly ash possesses good pozzolanic activity compared to that of alumino-silicate glass

of low calcium fly ash. The silicate-iron glass or iron glass which may also present in some fly ashes are either inert or very slow in pozzolanic reactivity.

The long term strength gain (self hardening) depends upon glassy phase and free lime content. The free lime present in fly ash is probably in intimate contact with fly ash particles and affects the strength development (Sherwood & Ryley;1966). There is a direct correlation between % of free lime and 28 day unconfined compressive strength depending upon carbon content(e.g. see Yudhbir & Honjo;1991).

The ashes of high carbon content have low pozzolanic activity.(Yudhbir & Honjo). In general the carbon in low calcium fly ash is more than that of high calcium fly ash. But the other factor that decides the quantity of carbon is the efficiency of plant (Diamond ;1984).

1.2.5 Classification schemes of fly ash

ASTM has classified the fly ash into two categories: Class F having $SiO_2+Al_2O_3+Fe_2O_3>70\%$ and Class C having these contents >50%. Mehta(1979) has proposed another classification based on the % of CaO: High calcium fly ash(CaO>15% and Low calcium fly ash Cao<5%. Other classifications given by Voina & Todar(1979) and Yudhbir & Singh(1991) based on chemical analysis mainly are basically similar. Later Yudhbir & Honjo (1991) have proposed another classification system based on CaO content and residual carbon, where in, the nature of minerals present and the glass content are also considered. Based on rate of gain of strength with curing time, Yudhbir and Honjo(1991) have suggested three categories of fly ashes which show different reactivity when treated with lime. Free lime

content and the amount of residual carbon distinguish reactive behavior of fly ashes in each categories.

The brief literature review focuses on the intimate relationship between quality of fly ash and it's chemical,mineralogical (specially glassy phase and reactive minerals) composition. Usefulness of X-ray diffraction,SEM, EDX techniques for detailed investigation of nature of fly ash has been highlighted.

1.3 Scope of present study

In this present study X-ray, SEM and EDX techniques have been employed to investigate some Indian fly ashes,both low and high calcium varieties. In order to investigate use of fly ash as a construction material for embankment and reclamation fills, limited studies have been conducted on compaction, consolidation and unconfined compressive strength characteristics of some of these fly ashes. The results have been compared with those reported in literature.

CHAPTER II

Materials Used and Tests Performed

2.1 Materials used

The fly ashes investigated in this study were taken from th boiler hoppers of four thermal power station .The fly ashes fro Choudwar(Cuttack), Parichha(Jhansi) and Panki(Kanpur) were of lo calcium variety. The fly ash from Neyveli lignite corporation was o high calcium variety. The location of the thermal power stations ha been given in fig-1. The fly ashes for low calcium variety wer resulted from the burning of hard coal. The high calcium Neyveli fl was resulted from the burning of lignite.

So far as known the use of these low calcium is almost nil or limited. It is being reported that the Parichha fly ash is being as admixture in blended cement whereas the Panki fly is sometimes used for reclamation fill. But the various use of Neyveli fly ash e.g. admixture in cement, soil stabilization, embankment construction, pavement construction etc have made this fly ash demanding. The materials were studied without any preprocessing such as drying, grinding and sieving. The grain size distribution of the ashes are given in fig-2. Some of the physical and chemical characteristics of these fly ashes are as follows:

Physical Properties	Fly Ash			
	Choudwar	Parichha	Panki	Neyveli
Color	Black	Grey	Grey	Grey
Specific gravity	2.30	2.14	2.19	2.62
pH(soil:water =1:2)	-	-	6.01	8.7
D_{50}	0.024μm	0.11μm	0.016μm	0.02μm

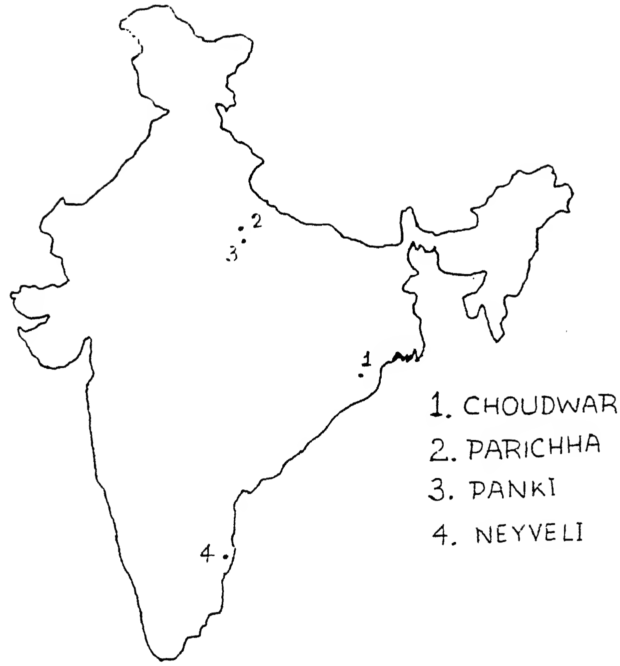


Fig 1. Location map of fly ashes tested

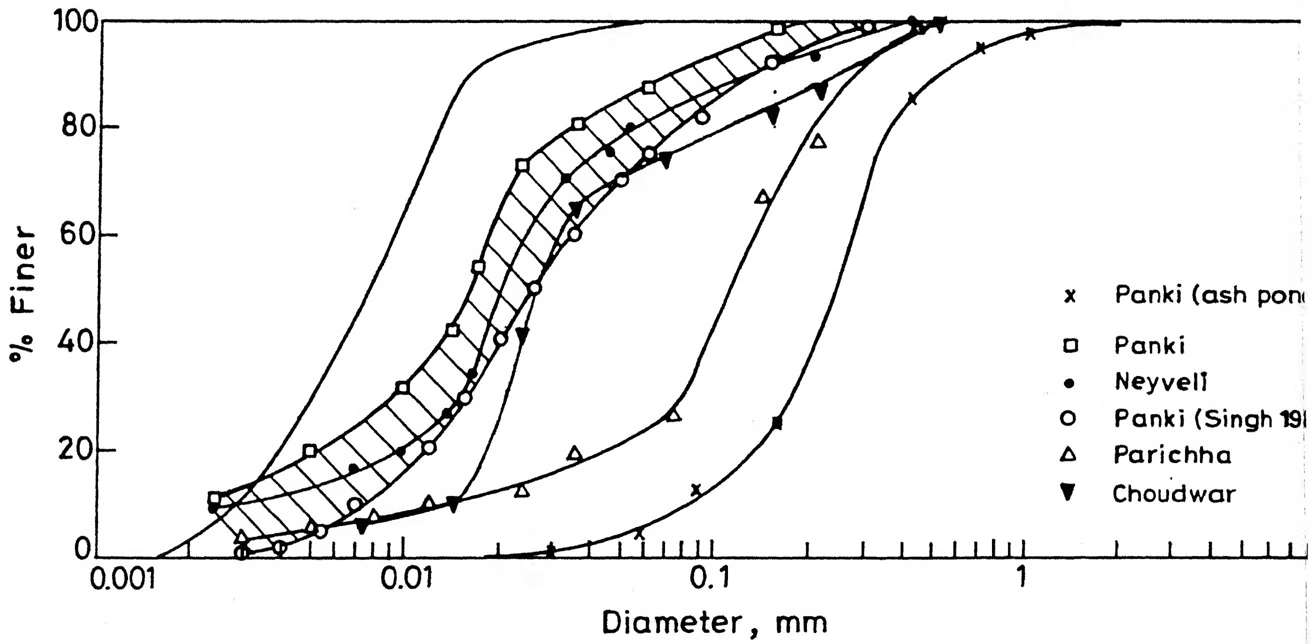


Fig-2 Particle Size Distribution of Fly Ashes

Chemical Properties	Parichha	Panki (i)	Panki (ii)	Neyveli (i)	Neyveli (ii)
SiO_2	59.94	65.1	62.0	24.8	28.0
Al_2O_3	17.93	26.0	28.4	29.0	22.5
Fe_2O_3	7.8	4.0	4.8	24.0	27.6
CaO	1.44	2.2	2.6	15.9	17.8
MgO	0.48	0.3	0.4	1.0	0.7
TiO_2	-	0.5	0.45	0.6	0.5
SO_3	0.42	0.3	0.25	1.1	0.95
$Na_2O + K_2O$	0.52	-	-	-	-
C (LOI)	8.22	2.5	2.6	1.4	1.5

2.2 Test techniques and sample preparation

In this study main emphasize was on the study of morphology, chemistry and mineralogy of fly ashes. The morphological investigation was conducted using both optical and scanning electron microscope . The quantitative assessment of whole fly ash its floaters and individual, particles were done with help of Energy Dispersive X-Ray (EDX) analysis. The qualitative analysis of crystalline and glassy phase was done by X-Ray Diffraction (XRD) analysis.

As a part of engineering characteristics of fly ashes, the grannullometry was determined by both Hydrometer analysis (following ASTM specification) and by Coulter Counter method.

2.2.1 Optical microscope

In this study Zeiss model optical microscope was employed using both analyzer and polarizer. The powder fly ash sample was well dispersed over a glass slide with help of polar liquid acetone or

methanol.Then this glass slide was put under the light and t specimens were observed at different magnifications and then thes were photographed.

2.2.2 Scanning electron microscope (SEM)

Principle : The basic principle of the scanning electro microscopy is to scan a specimen with a finely focused beam o Kilovolt energy. An image is formed by scanning cathode ray tube i synchronism with the beam and by modulating the brightness of thi tube with beam excited signals. In this way an image is built u point by point which shows the variation in the generation an collection efficiency of choosen signals at different points on the specimen. By using different condition and specimens, it is possible to obtain image showing the surface topography, surface potential distribution, magnetic domains, crystal orientations and crystal deffects in specimen. The detail about operation of SEM has been described else where.(Goodhew and Humpbrey; 1988).

2.2.3 Energy Dispersive X-ray (EDX) analysis

Principle:When a gun electron of electron bombards the sample to be studied, X-ray spectrum is emitted by the sample. Measurement of the energy spectrum of the characteristics X-ray that are emitted determines the elements that are present in the specimen. The concentration of an element in the specimen C_{spec} is given by

$$C_{spec} = \frac{N_{spec}}{N_{std}} \cdot Z \cdot A \cdot F \cdot C_{std}$$

where,

C_{spec} = concentration of the element in the sample.

C_{std} = accurately known concentration of this element in the standard

standard

N_{spec} = number of characteristic X-ray counts from the specimen in fixed time interval

N_{std} = number of characteristic X-ray counts arriving from a standard of known composition in a similar time

Z, A and F are the corrections for the atomic number, absorption and fluorescence respectively. Use of these corrections are commonly known as the ZAF technique. These calculations and corrections are performed efficiently by a computer programme. In this study Quantex-V programme was employed for this purpose. In practice the results are recorded in terms of energy of characteristics X-ray emitted. The relative percentage of the elements, present in the sample corresponds to the peak area under that element.

2.2.4 X-Ray Diffraction (XRD) Technique

The basic principle underlying the identification of minerals by XRD technique is that each crystalline substance has its own characteristics atomic structure which diffracts X-ray with a particular pattern. In practice, the diffraction peaks are recorded on output chart in terms of 2θ, where θ is the glancing angle of X-ray beam. The 2θ values are then converted to lattice spacing 'd' in angstrom unit using Bragg's law

$$d = \frac{\lambda}{2n \sin\theta}$$

where,

n is an integer

λ = wave length of X-ray specific to target used

2.3 Sample preparation and test condition

The method of sample preparation and test condition for above tests are depicted below.

2.3.1 Sample preparation for Coulter counter method

A 10-20 mg of sample after passing through 75μm sieve dispersed in suitable electrolyte. In general, water insoluble materials are dispersed in aqueous electrolyte such as 1% W/V sodium chloride or 5% trisodium phosphate solution. But water soluble materials are dispersed usually with 5% W/V lithium chloride in methanol or 5% ammonium thiocyanate in isopropanol. So for Neyveli fly ash 5% lithium chloride in methanol was taken as electrolyte while for other low calcium fly ashes 1% W/V sodium chloride in aqueous solution served as electrolyte. This dispersed sample was kept in a glass beaker, which is then placed for the test and continuously stirred to avoid agglomeration. The details about the operation and calculation technique have been described elsewhere (see instruction manual, Coulter Counter, Z_B model).

2.3.2 Sample preparation for SEM and EDX

As the main objective for use of this tool was to find out the morphology and chemical composition of individual particles and fractions, the sample was well dispersed over a copper copper or brass stub followed by silver coating for morphological analysis and carbon coating for chemical analysis. This study was conducted in a Jeol 840-A model SEM fitted with EDX analysis.

The working conditions for the study were as follows:

1) working distance = 15 mm

2) Probe current = 10^{-11} to 10^{-9} amp

3) accelerating voltage = 20 Kv

4) absorption energy = 10.23 Kev

5) counting time = 100 s

2.3.3 Sample preparation for XRD analysis

The powder sample was placed in a sample holder of size 3cm x 3cm with 2mm thick. Then the surface of sample was smoothen with glass plate. With the help of spring clip the sample holder was place in front of X-ray. X-ray diffraction analysis for this study was performed on a Rich-Siefert X-ray diffractometer using copper target and Ni-filter. For reason of consistency the following conditions were maintained through out the study.

1) Input energy = 20 m Amp , 30 Kv

2) Scan speed = 1.2°/min

3) Angle scanned = 8° to 52° (2θ)

The minerals were identified in accordance with Joint Committee on Powder Diffraction Standard (JCPDS) mineral and inorganic powder diffraction files.

CHAPTER III

Test Results and Discussions

In this chapter results of experimental investigations(Table-3) carried out in this study will now be presented. First of all morphological,chemical and mineralogical characteristics of fly ashes studied will be evaluated and the results will be compared with the data reported in literature.

Results of grain size, compaction, consolidation and unconfined compression tests will then be presented and the trends compared with established relationships reported in literature. Gain in compressive strength with time will be compared with the patterns suggested by Yudhbir & Honjo (1991).

3.1 Morphological characteristics

3.1.1 Optical microscopic investigations

Parichha,Panki and Neyveli fly ash sample s were studied under optical microscope using both analyzer and polarizer. Fig-3 depicts the results for Parichha fly ash samples.Fig-3(a) depicts the form of residual carbon particles in the ash which were separated by suspension in water. The residual carbon particles are solid,irregular in shape,black in color and vary in size from 300μm to 800μm.

Microscopic study of fly ash fraction > 75 μm is given in fig-3(b). Predominance of quartz particles and magnetic spherical particles is observed. Quartz particles are angular, colorless, crystalline solids(50-70μm) where as the magnetite is seen as spherical light brown to black particles. (30-50μm).

TABLE 3(a)

PROPERTIES	TECHNIQUES	NO. OF TESTS Choudwar	NO. OF TESTS Parichha
Grannulometry	1. Hydrometer	1	1
	2. Coulter Counter	1	1
Specific Gravity	ASTM	1	1
Morphology	1. Optical Microscope	-	3
	2. SEM		
	Whole Fly Ash	3	2
	Floater	1	2
	Residual Carbon	2	2
Chemistry	1. Chemical Extraction	-	1
	2. EDX		
	Whole Fly Ash	1	2
	Floater	2	2
	Individual particle	1	3
Mineralogy	XRD		
	Whole Fly Ash	1	1
	Floater	1	1
	Diff. Fraction	-	2
OMC and $\gamma_d max$	Havard Miniature	-	1
Strength	Unconfined Compression	-	9

TABLE 3(b)

PROPERTIES	TECHNIQUES		NO. OF TESTS Panki	Neyveli
Grannulometry	1. Hydrometer		1	1
	2. Coulter Counter		1	1
Specific Gravity	ASTM		3	3
pH	pH Meter		1	1
Morphology	1. Optical Microscope		2	2
	2. SEM			
		Whole Fly Ash	3	4
		Floater	1	1
		Residual Carbon	1	1
		Magnetic Particles	-	4
		HCl Treated	-	4
		HF Treated	4	2
		Hydrated	-	1
Chemistry	1. Chemical Extraction		1	1
	2. EDX			
		Whole Fly Ash	3	2
		Floater	1	2
		Individual particle	-	2
		Diff. Fractions	2	3
		HCl Treated	-	3
Mineralogy	XRD			
		Whole Fly Ash	1	1
		Floater	1	2
		Diff. Fraction	2	4
		Hydrated	2	3
		Burnt Fly Ash	2	-
OMC and $\gamma_d$max	Havard Miniature		1	1
Strength	Unconfined Compression		10	8

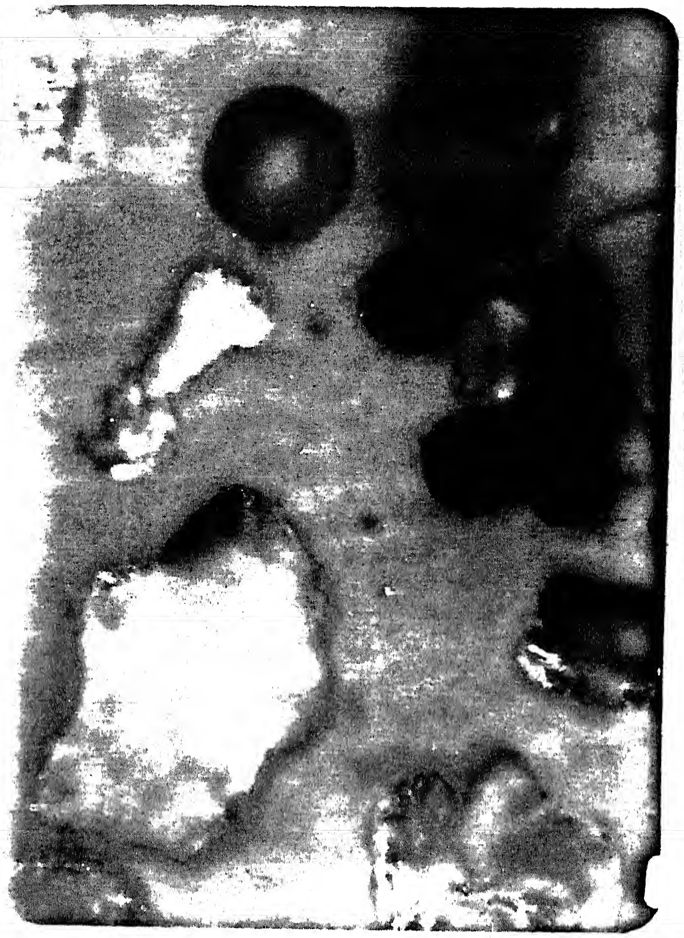
Floaters of Parichha was separated from water suspension of fly ash and the nature of these particles is shown in fig-3(c). Under the microscope the cenospheres seen as four spherical particles in fig-3(c)(the yellowish tinge appears due to the background of the photograph) appears white in reflected light. These are spherical particles of glassy solid and are approximately 150-200μm in diameter. The dark particles are grains of residual carbon.

Fig-4(a) shows the types of particles in Panki fly ash fraction >75μm. There are colorless, angular to sub angular quartz grains,(100μm), agglomerated irregular solid particles showing varied colors in reflected light(150-360μm), light colored glassy solid rounded particles(180μm) and irregular residual carbon particles in this fraction. Results from <75μm fraction are shown in fig-4(b). The small spherical particles white in reflected light are cenospheres.

In case of Neyveli fly ash the magnetic particles in fly ash were separated and these shown in fig-5(b). Except for few agglomerated particles, the magnetites are light to dark brown spheres. The >75μm fraction contains reddish hematite, colorless sub angular quartz, light to dark brown spherical magnetite and dark irregular residual carbon particles.

These limited optical studies give morphological characteristics of these three fly ashes which are similar to the detailed results reported by Watt and Thorne(1965).(Table-1).

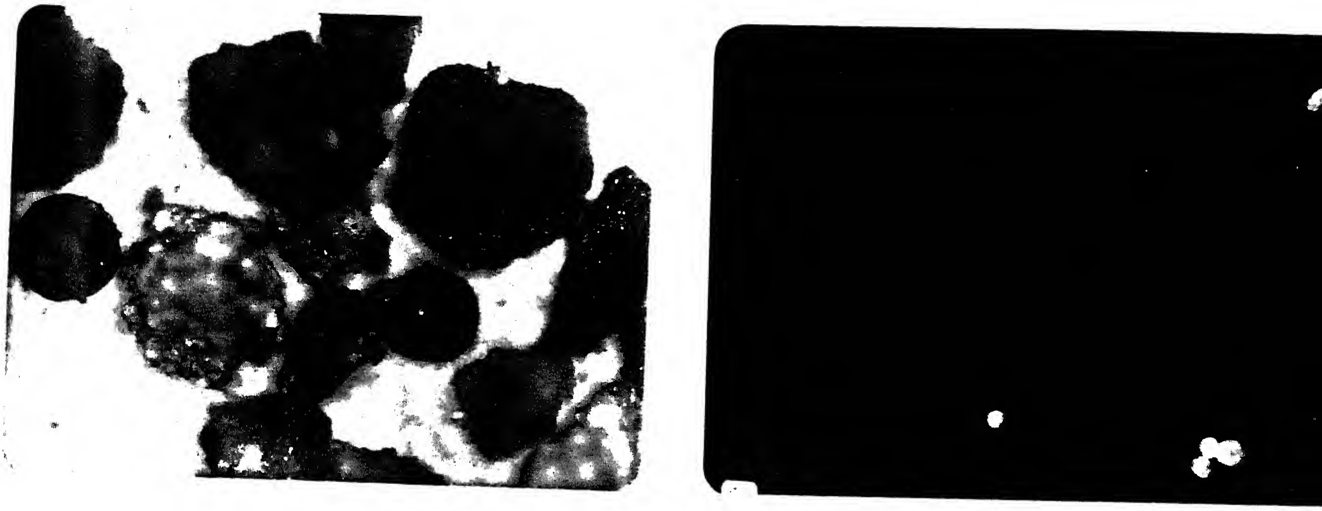
(a) 200µm



(b) 50 µm

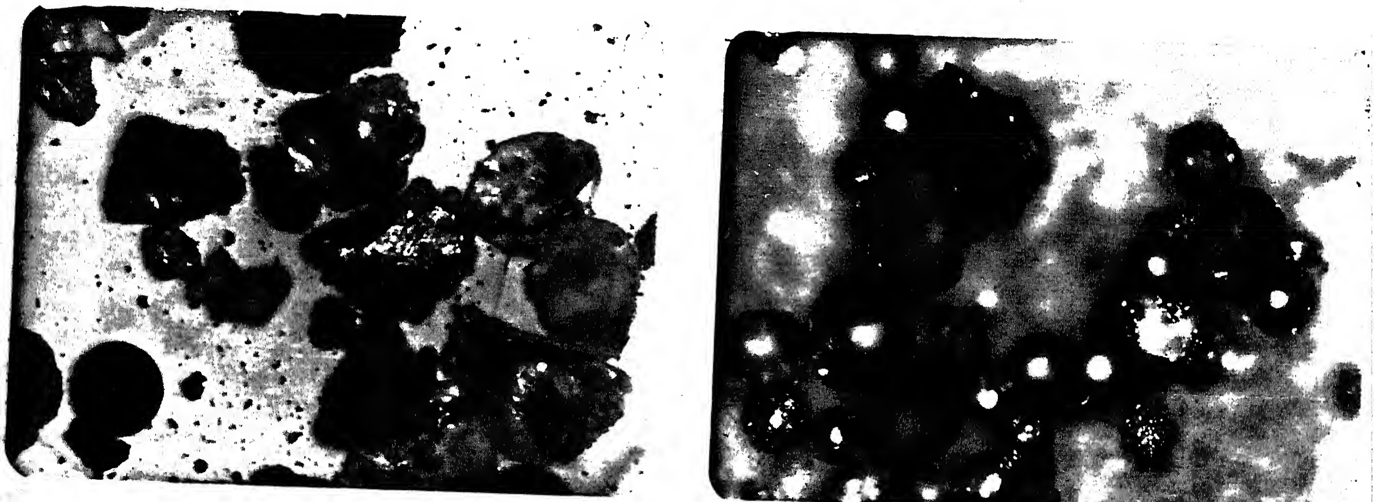
(c) 100 µm

Fig-3 Optical photomicrograph of Parichha fly ash



(a) 100 µm (b) 100 µm

Fig-4 Optical photomicrograph of Panki fly ash



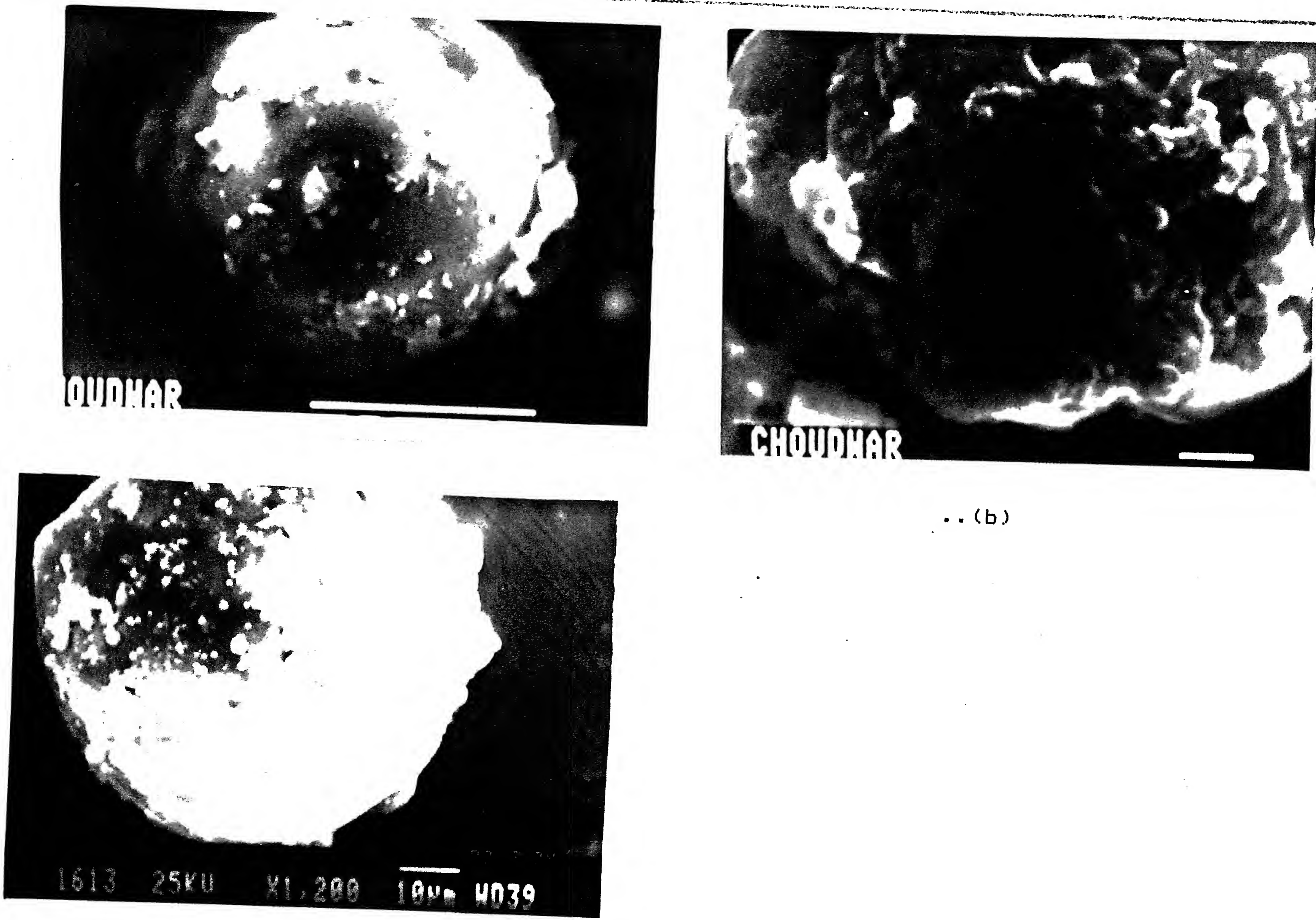
(a) 100 µm (b) 100 µm

Fig-5 Optical photomicrograph of Neyveli fly ash

3.1.2 Scanning electron microscopic investigation

In the present study major emphasis was on scanning electron microscopic study than optical microscopic investigation.Fig-6(a) and 6(b) show scanning electron micrographs for the Choudwar fly ash where 6(c) depicts a cenosphere in the floaters collected from water suspension. Fig-6(b) shows irregular residual carbon with some small spherical embedded particles. The surface of the spherical particles in fig-6(a) and 6(c) are coated with small fragments and tiny spherical particles. These coating could results from condensation and solidification of Si and Al as reported by Fischer and Natusch(1979) for low calcium fly ash. Morphological forms of Parichha was depicted in fig-7. Fig-7(a) and fig-7(b) show typical morphology of iron rich spherical particles. Fischer and Natusch(1979) also reported similar morphology for low calcium fly ash. Floaters of Parichha were collected from water suspension and fig-7(c) shows a cenosphere with tiny holes on the surface and fig-7(d) depicts a spherical particles with large number of surface droplets resulting from condensation and solidification of inorganic substances and are rich in Si and Al.(see Fischer and Natusch; 1979).

Panki fly ash micrographs are depicted in fig-8. The typical spherical shaped particles of varying size of low calcium fly ash are shown in fig-8(a) and fig-8(b)(see Diamond; 1986) where as a plerosphere is observed in fig-8(c). Though it is not very clear from the photomicrograph, the plerosphere, as seen in screen of SEM, contains rod shaped particles(possibly mullite), this is so



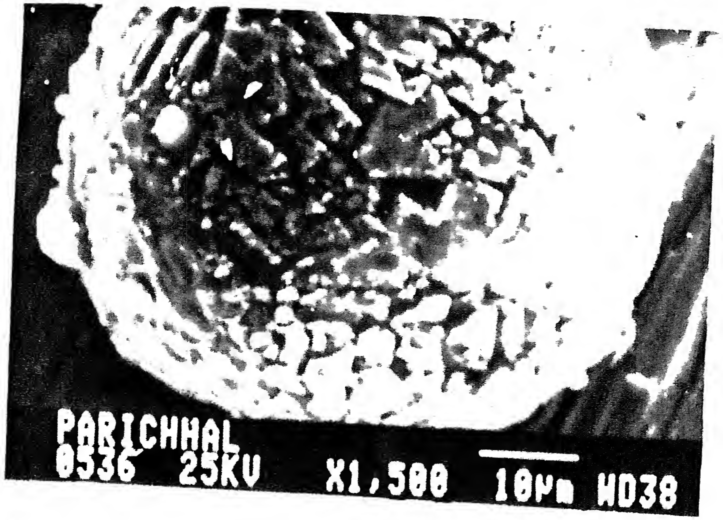
(a)..

..(b)

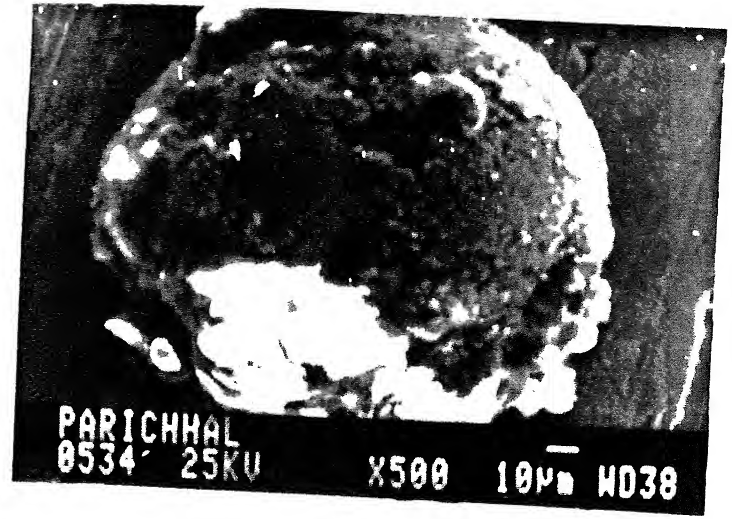
..(c).

Fig-6 Morphological characteristics

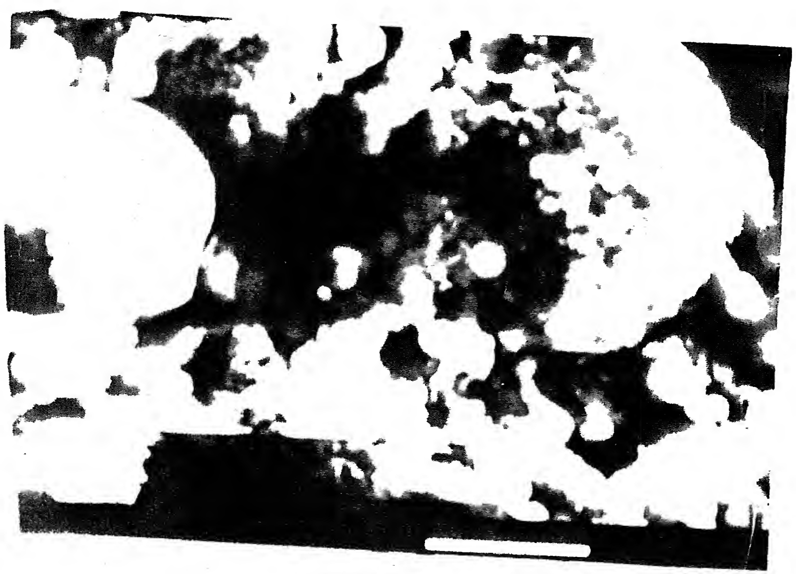
(a)..


PARICHHAL
0536 25KV X1,500 10μm WD38

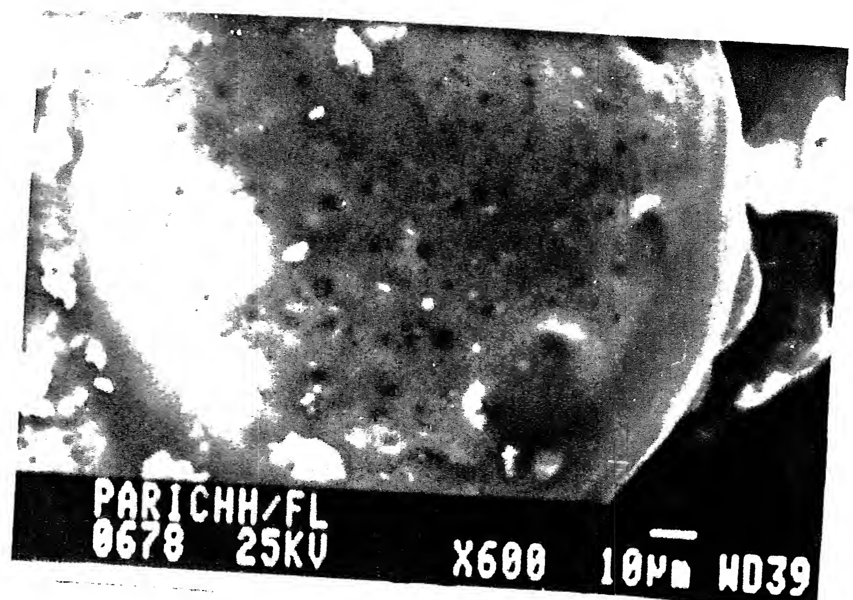
..(b)..

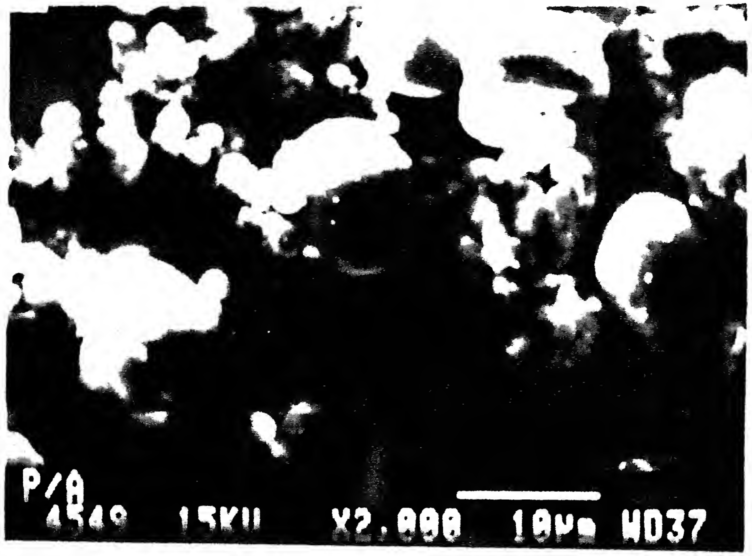

PARICHHAL
0534 25KV X500 10μm WD38

(d)

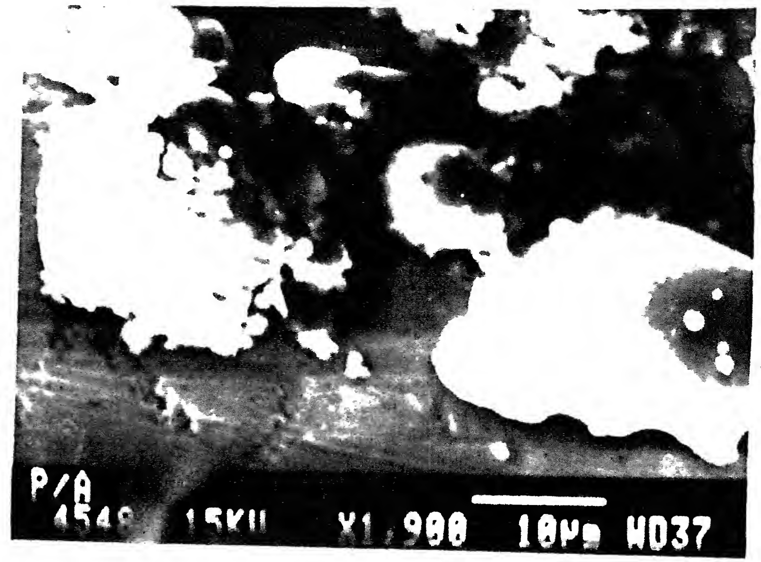


.(c)..


PARICHH/FL
0678 25KV X600 10μm WD39


P/A
4549 15KV X2,000 10μm WD37

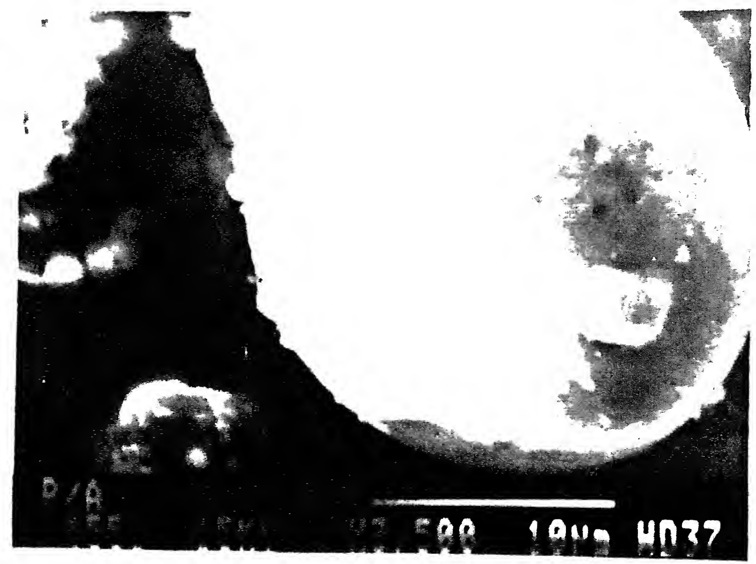
(a)


P/A
4549 15KV X1,900 10μm WD37

(b)


P/Ceno
4640 25KV

(d)


P/A
10μm WD37

(c)

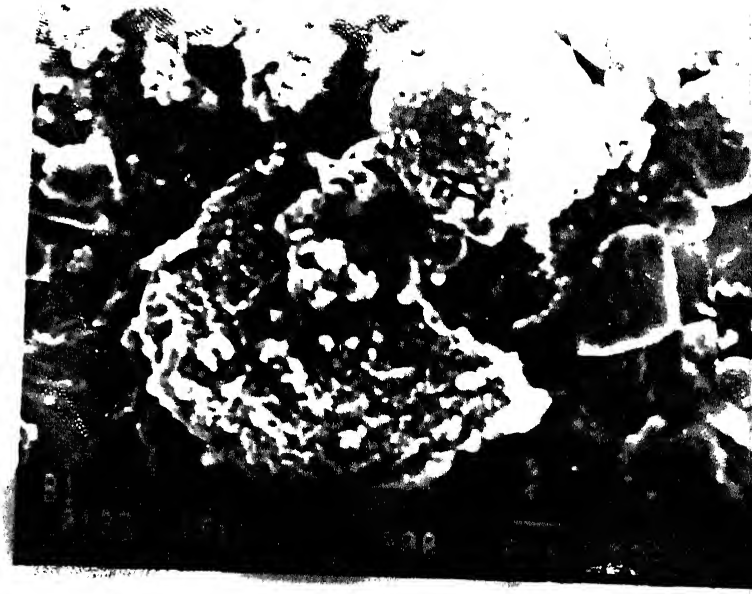
confirmed after treatment of this fly ash as discussed later.(fig-14). Fig-8(d) shows a cenosphere as observed in floaters of this fly ash. Once again a few coatings of condensed and solidified Si and Al can be seen on this fly ash particle.

High calcium Neyveli fly ash micrographs are depicted in fig-(9). Two spherical particles with extensive calcium coatings are shown in fig-9(a)(see Gay and Frigge;1988) whereas agglomerated particles are depicted in fig-9(b) and fig-9(c).

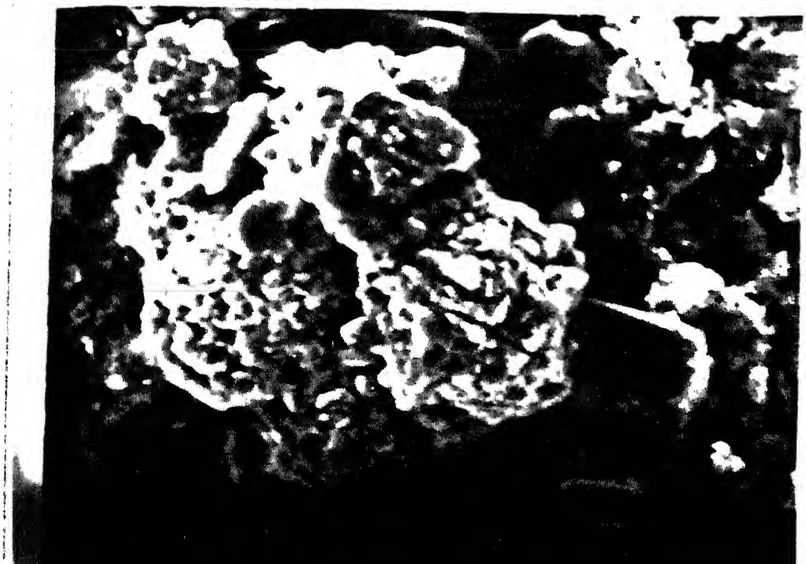
Different forms of residual carbon in these fly ash samples are indicated in fig-10. It will be seen that carbon particles are irregular in shape and may have embedded spherical particles of various sizes.(see fig-10(b)).

Diamond(1986) has characterized low calcium fly ash with a swiss cheese like morphology of residual carbon. Fig-11(a) and fig-11(b) show similar morphological features for Choudwar(upper right hand corner) and Panki fly ash respectively. Similarly cluster arrangement of small spherical particles is suggested (Diamond;1986) as a typical morphological feature. Fig-12 shows such forms for Panki (low calcium fly ash; fig-12(a)) and Neyveli (high calcium fly ash; fig-12(b)). According to Diamond(1986) such arrangements may result, from spheres bound together either by fused glass contact or by thin layer of unburned carbon retained between them. In this study, Panki fly ash which has relatively high carbon content as compared to Neyveli was treated with HydroFlouric (HF) acid and then micrographed. Some of the clustered arrangements were still present after treatment as shown in fig-12(a). Since the treatment with HF

(a)..

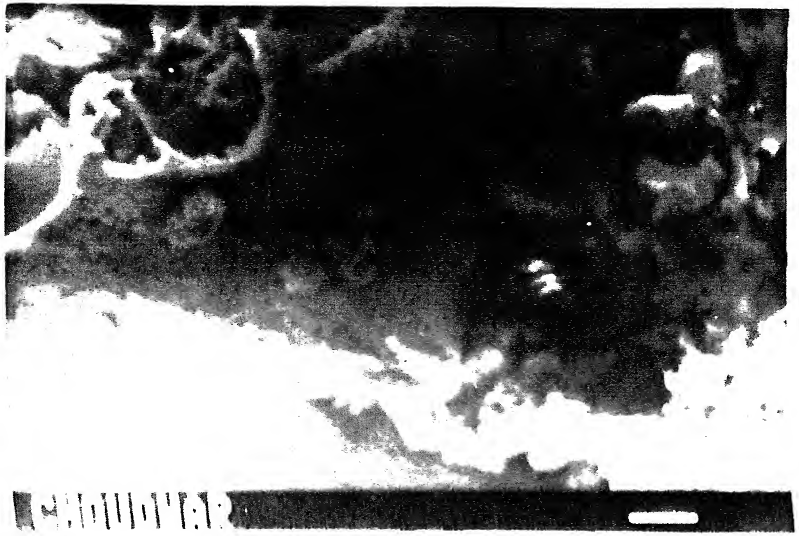


..(b).

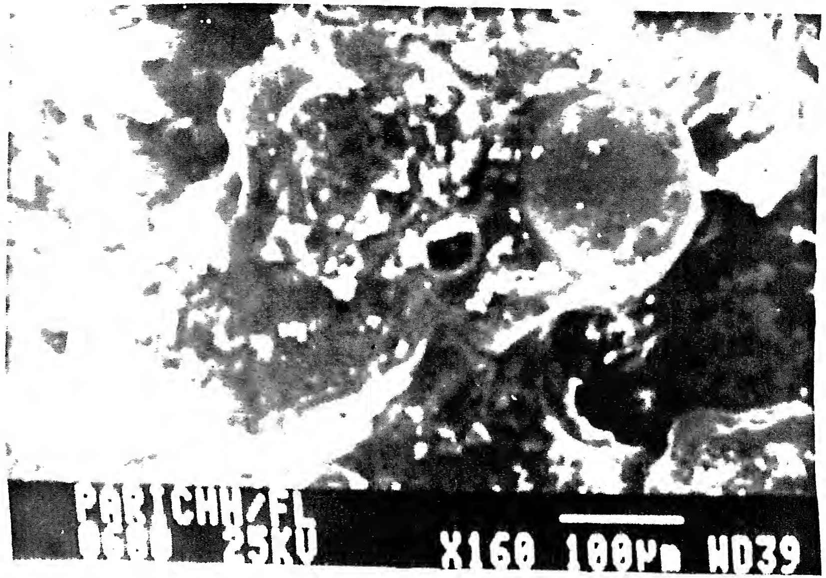


...(c)

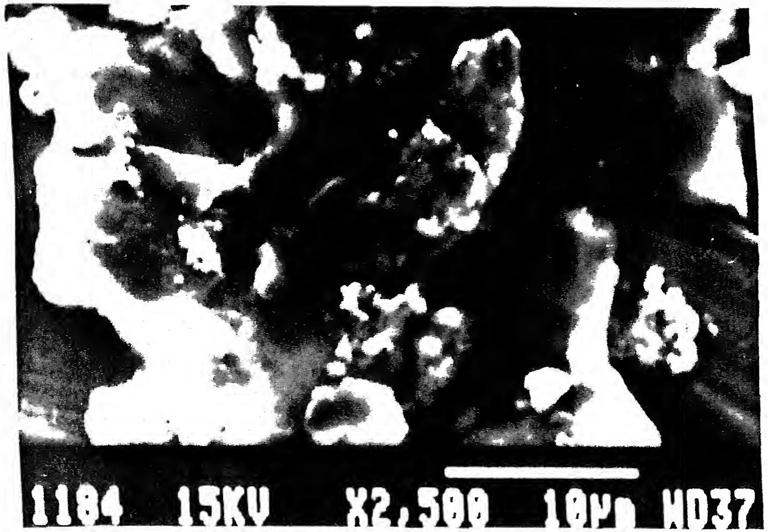
Fig-9 Morphological characteristics of Neyeveli



(a).



...(b).



..(d)

..(c

Fig-10 Morphological of residual carbon particles in fly ash

(a).

..(b)..

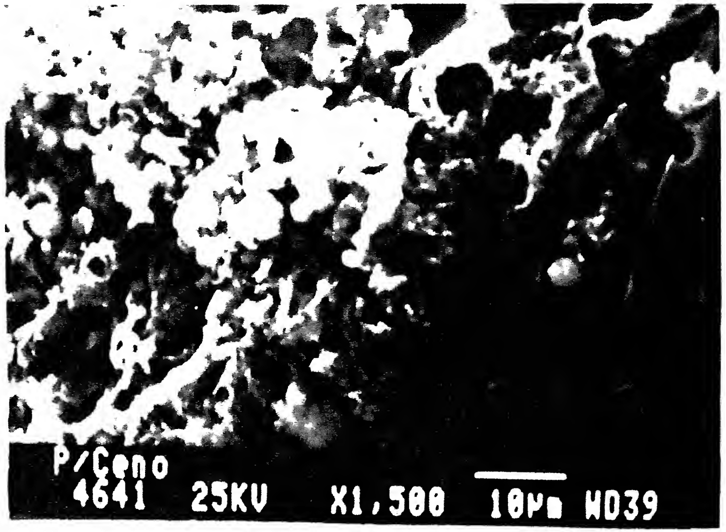
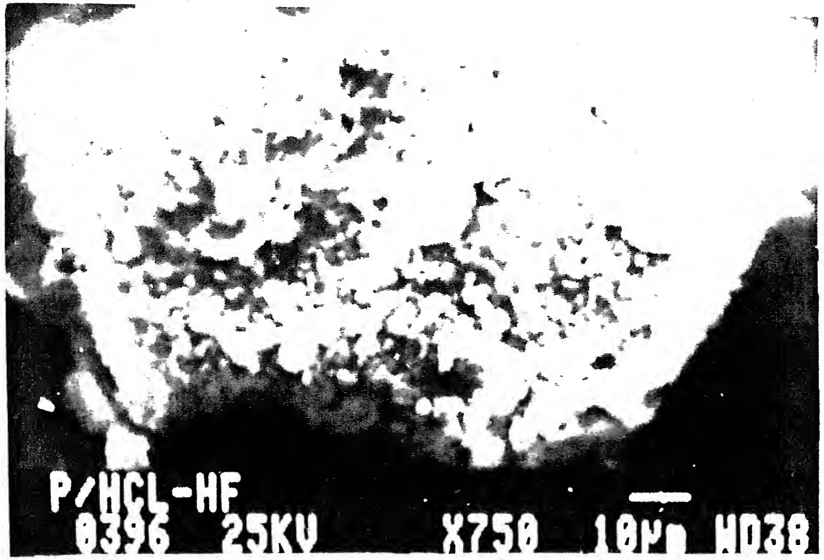


Fig-11 Swiss cheese like morphology of residual carbon embedded with fly ash tiny particles.

(a).



..(b)..

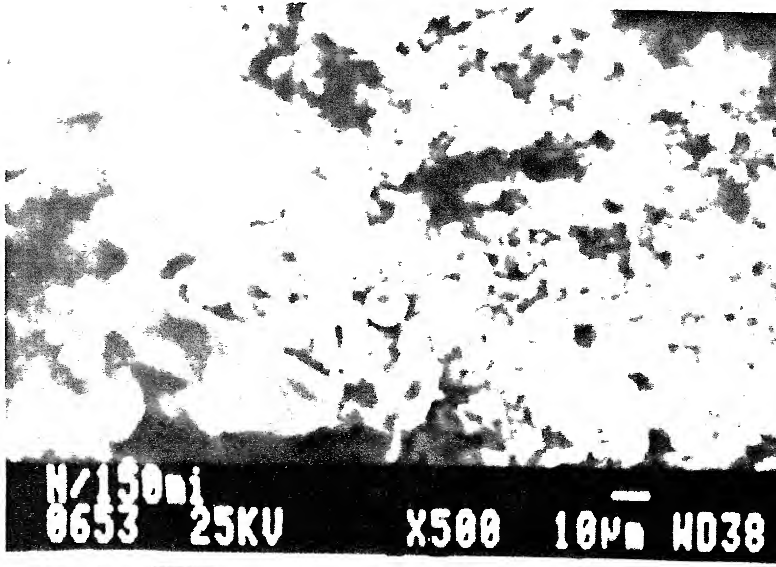


Fig-12 Cluster arrangement of fly ash particles

would have dissolved glass contact, it would seem the spherical particles for Panki fly ash bound together by thin layer of carbon as suggested by Diamond(1986). In case of high calcium Neyveli fly ash the clustered arrangement shown in fig-12(a) was not observed after the fly ash was treated with acids(HCl and HF) thus suggesting fused glass contacts in case of high calcium fly ash.

The iron rich fly ash particles have a typical morphology showing a structure comprised ofsmall triangular platy pieces fitted together (Diamond;1986). Fig-13 shows morphology of iron rich particles of Neyveli fly ash. Fig-13(c) is an enlargement of the surface of the particle shown in fig-13(b). The stacked plate are iron rich. In fig-13(d) two magnetic spheres with variable surface texture are depicted for this fly ash. The smooth surfaced magnetic spheres may have a thin glass coating, which when dissolved by treatment with HF acid or by mechanical impact would display the typical iron spinel morphology. Diamond(1986) reports that after treatment with HF of magnetic particles, a typical morphology indicating a plate structure is revealed. Similar result was obtained in this study as shown in fig-16.

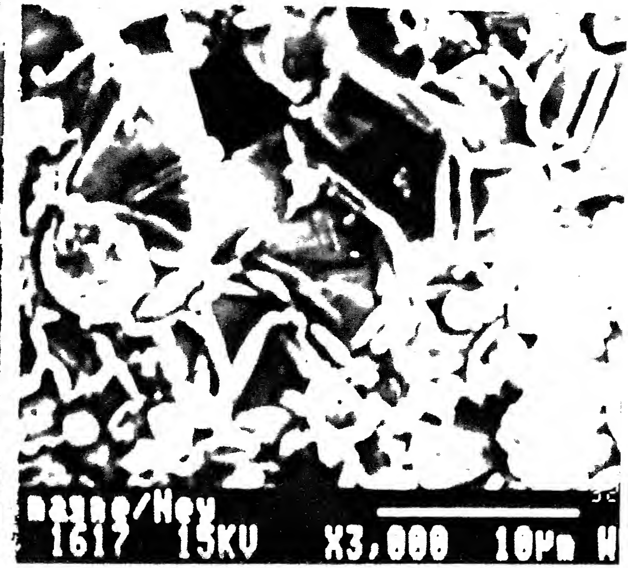
In order to investigate the internal structure of low calcium Panki fly ash particles, it was treated with HF and the results of SEM are shown in fig-14. Presence of a needle like mullite crystal, arranged as a frame work of a sphere was revealed as shown in fig-14(a) and fig-14(b). Diamond(1986) reports similar finding for a low calcium fly ash. Fig-14(c) shows a particle where the acid treatment was incomplete and only a faint appearance of the


ne/Ney
18 15KU X450 10μm WD23

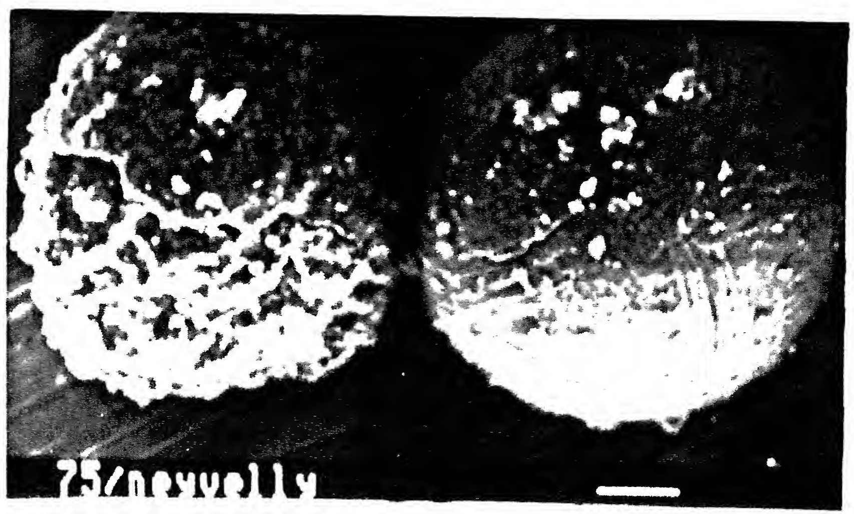
(a)...


magne/Ney
1616 15KU X300 100μm WD23

..(b).

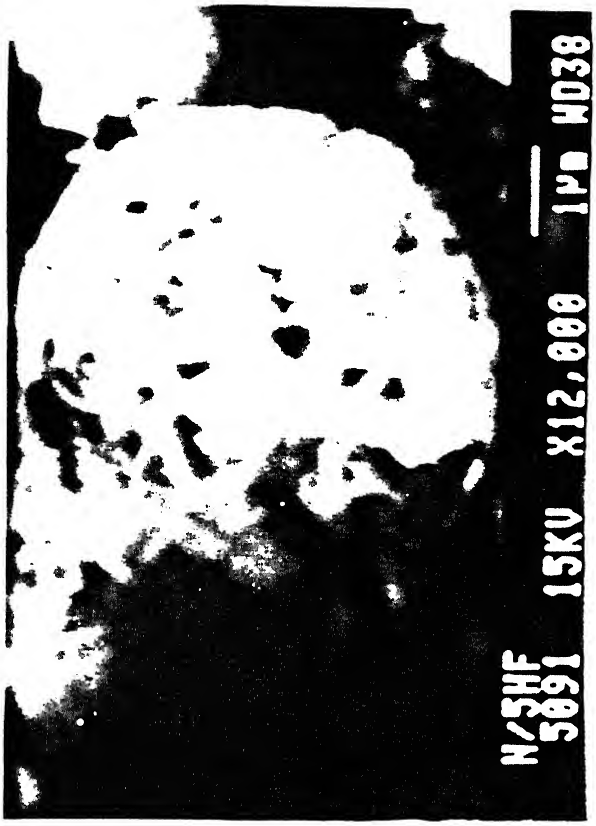

magne/Ney
1617 15KU X3,000 10μm

..(c).


75/neyvelly

...(d)

(a)



(c)

(b)

Fig-14 Morphology of HF treated panki fly ash.

underlying structure is suggested.

Results of acid treatment(HCl) for Neyveli are indicated in fig-15. While 15(a) shows a typical structure of an iron rich particle, fig-15(b) indicates a plerosphere consisting of Al and Si.Fig-15(c) shows a rare fly ash particle rich in Ti(see Fischer and Natusch;1979) and in fig-15(d) iron and aluminum rich particle is revealed after the dissolution of surface glass. In high calcium fly ash HCl dissolves calcium aluminate glass forming the outer layer of spherical particles.

As indicated earlier HF treated iron rich particles of high calcium Neyveli fly ash revealed typical morphology of iron particles indicated in fig-16.

A floater of Neyveli fly ash, after crushing in a ball mill, indicates a smooth inner layer under an outer cover as shown in fig-17. The surface coatings are rich in calcium .

High calcium fly ash shows increase in strength when cured with water due to the formation of ettringite. Neyveli fly ash in hydrated form after 28 days revealed a typical ettringite (hexagonal) morphology as shown in fig-18.

These investigation into the morphology of magnetic and non-magnetic fly ash particles and that of residual carbon reported here are shown to give results consistent with the finding of Diamond(1986),Fischer and Natusch(1979) for low calcium fly ashes. Results for one high calcium fly ash are presented here and typical morphological forms for the same have been indicated. The likely mechanism for clustered particles for low and high calcium fly ash

(a)

(b)

(d)

(c)

Fig-15 Morphology of HCl treated Neyeveli fly ash

(a)

(b)

Fig-16 Morphology of magnetic particles after 6hr HF treatment

Fig-17 Morphology of Neyveli floater showing layers of glassy phase

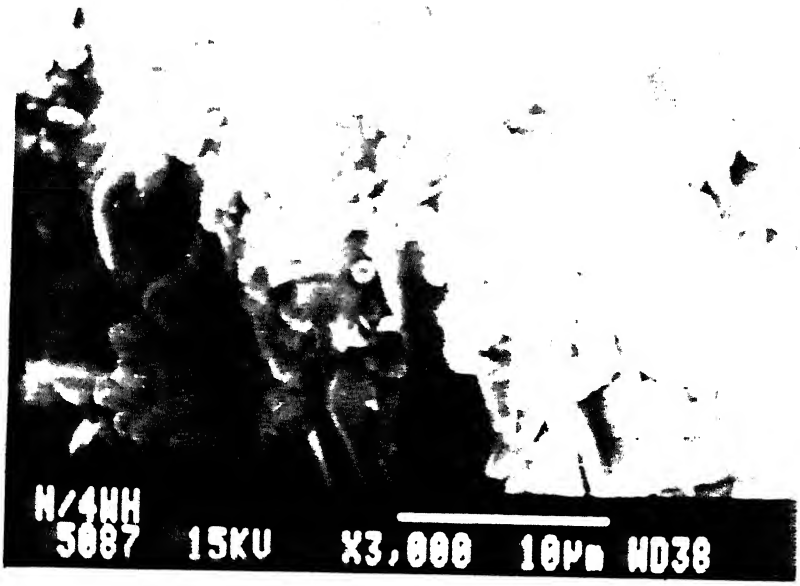


Fig-18 Morphology of hydrated Neyveli fly ash

are suggested as due to binding by thin layer of residual carbon in case of low calcium fly ash and due to fused glass to glass contact in case of high calcium fly ashes. The latter mechanism may also hold for some low calcium fly ashes with small carbon content. These mechanism were initially suggested by Diamond(1986).

3.2 CHEMICAL CHARACTERIZATION OF FLY ASH

Among the factors governing pozzolanic reactivity of fly ash, chemical composition of individual grains is of considerable importance. As discussed earlier,there are different methods of chemical analysis, most of which provides gross compositional analysis only without indicating the variation in chemical composition of individual grains.

EDX analysis on the other hand provides a promising tool to investigate chemistry of individual grains, the coatings over it for both crystalline and amorphous phases. Because of its capability to analyze micro sized particles and the coatings over it, EDX is also called micro-analyzer. In the following section, results of EDX analysis for four fly ashes, Choudwar, Parichha, Panki and Neyveli including their different fractions, floaters and particles with and without acid treatment are presented and the finding have been compared with those reported in literature especially for low calcium fly ashes. Due to the fact that Si and Al have their atomic number so close to each other, it is rather difficult to exactly quantify their percentage. Efforts to calibrate EDX for Si and Al content encounter these difficulties too. In this study only comparative results in forms of spectra are presented.

3.2.1 EDX spectra of whole fly ash

Fig-19, 20, 21 and 22 present EDX spectra for Choudwar, Parichha, Panki and Neyveli respectively. As will be seen Choudwar fly ash has practically no calcium where as Neyveli has very high calcium content; Parichha and Panki indicating intermediate results. While Choudwar, Parichha and Panki (fig-19, 20, 21) have similar proportion of Si and Al,Neyveli fly ash has comparatively much smaller Si and Al content. In the three low calcium fly ashes, viz. Choudwar, Parichha and Panki, Si content is roughly double of Al content where as it is just the opposite in case of high calcium Neyveli fly ash. The low calcium fly ashes have much high(Si and Al) content contrast to the high calcium fly ash, which would have classified the former as F type and the latter as C type by the ASTM classification standards. The other major constituents of low calcium fly ash are Fe, K, Ti and traces of S where as in case of high calcium fly ash these are Fe, S, Ti and traces of magnesium. Sulphur content in high calcium fly ash is much higher as compared to low calcium fly ashes where it is observed only as a trace.

3.2.2 EDX spectra of fly ash floaters

Floaters for low calcium fly ashes were collected from a water suspension and their spectra are indicated in fig-23,24 and 25 for Choudwar,Parichha and Panki respectively. While the Si and Al contents of floaters for all the low calcium fly ashes are similar to those of the whole fly ash sample. Choudwar floater shows spectra similar to that of the whole fly ash(fig-19). As will be discussed later, K content is indicative of amount of alumino silicate glass

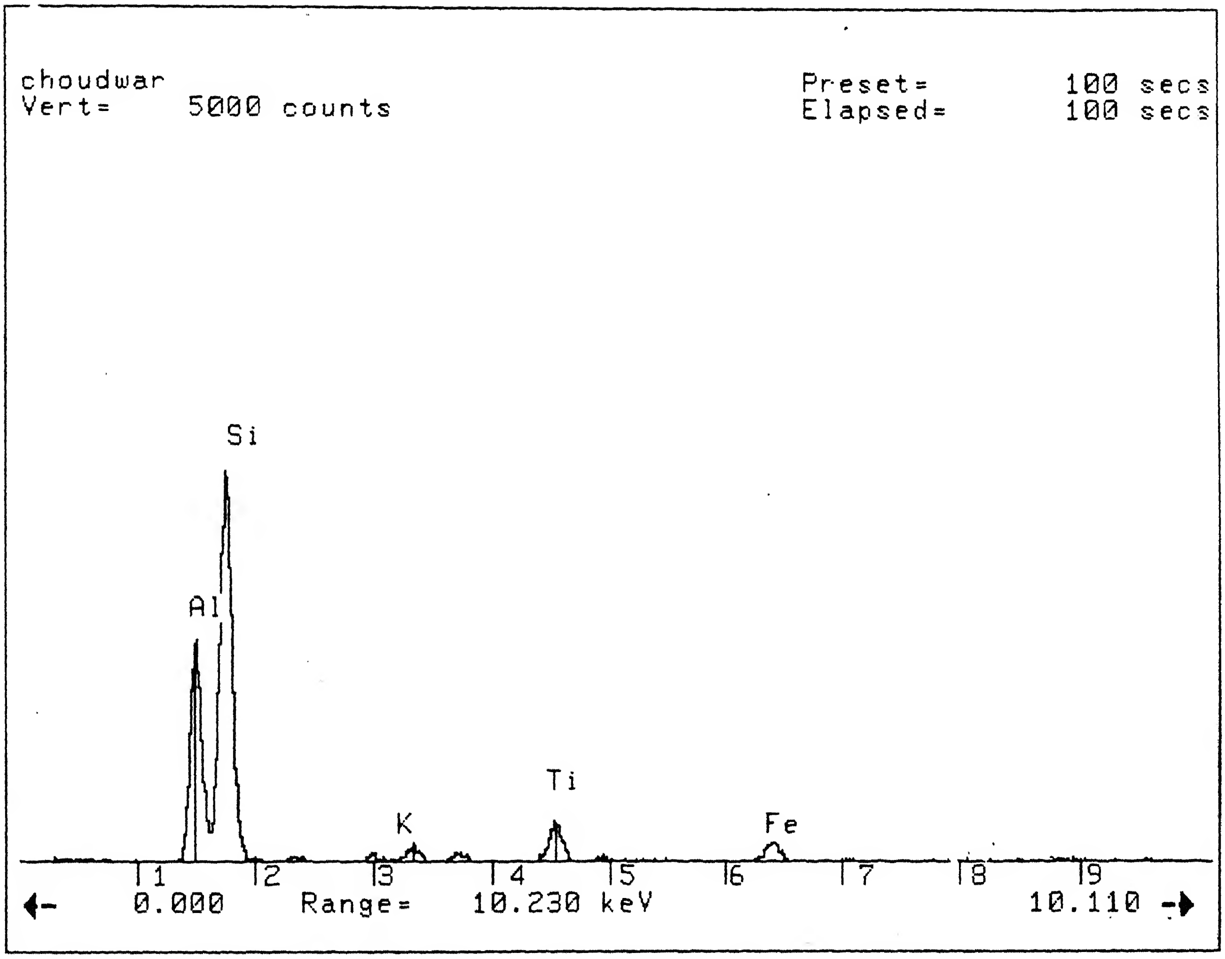


Fig-19 EDX spectra of choudwar fly ash

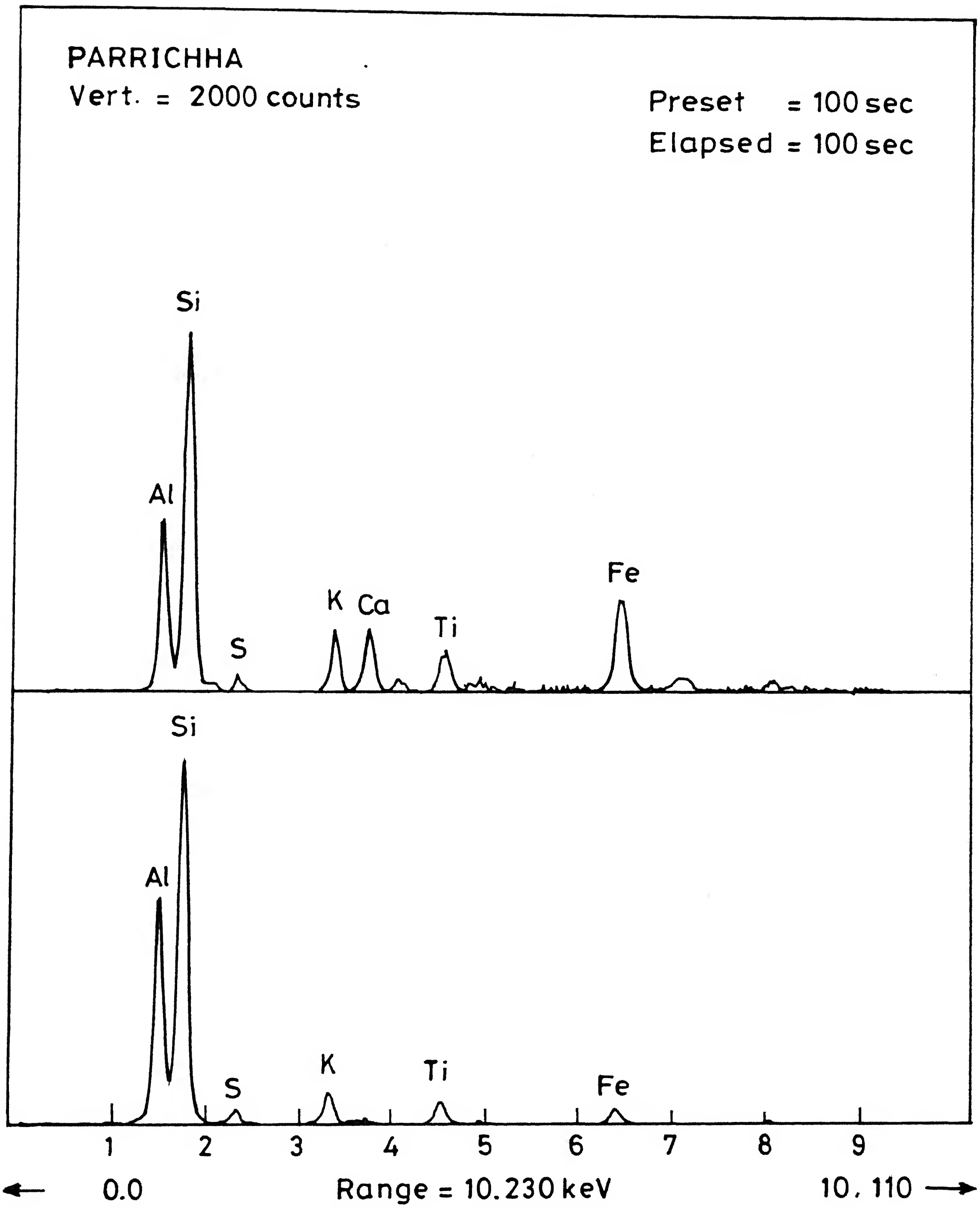


Fig-20 EDX spectra of parichha fly ash

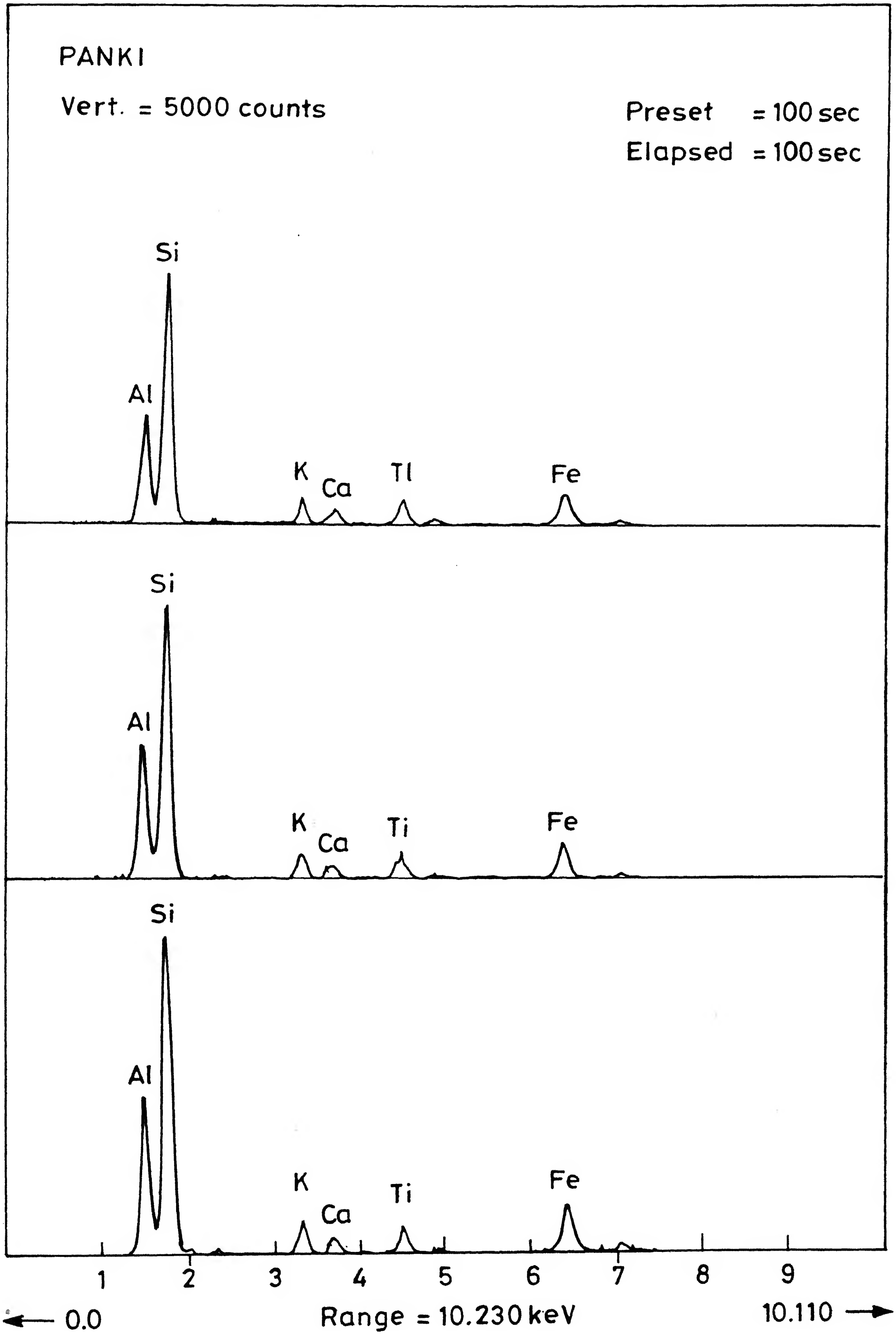


Fig-21 EDX spectra of panki fly ash

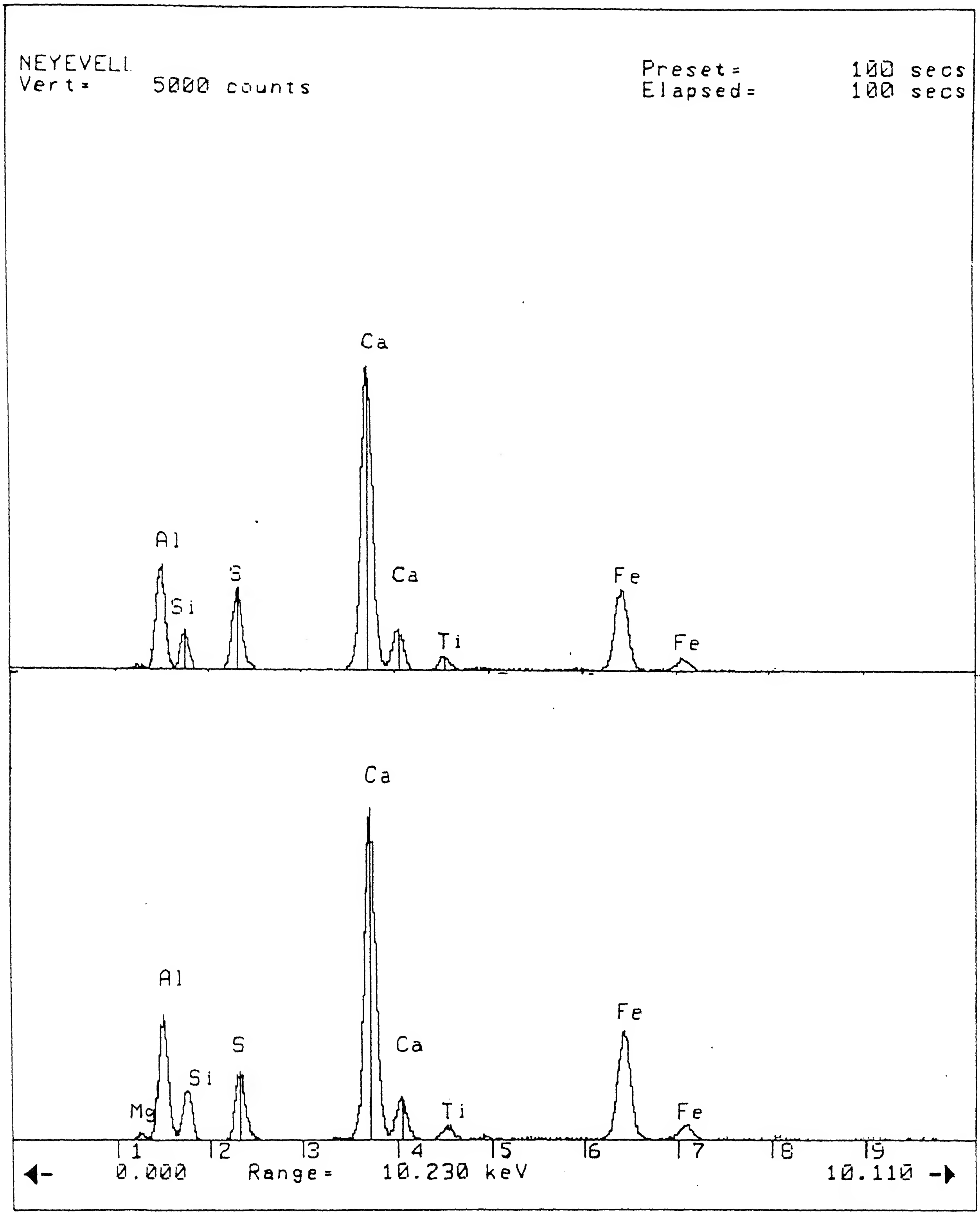


Fig-22 EDX spectra of Neyveli fly ash

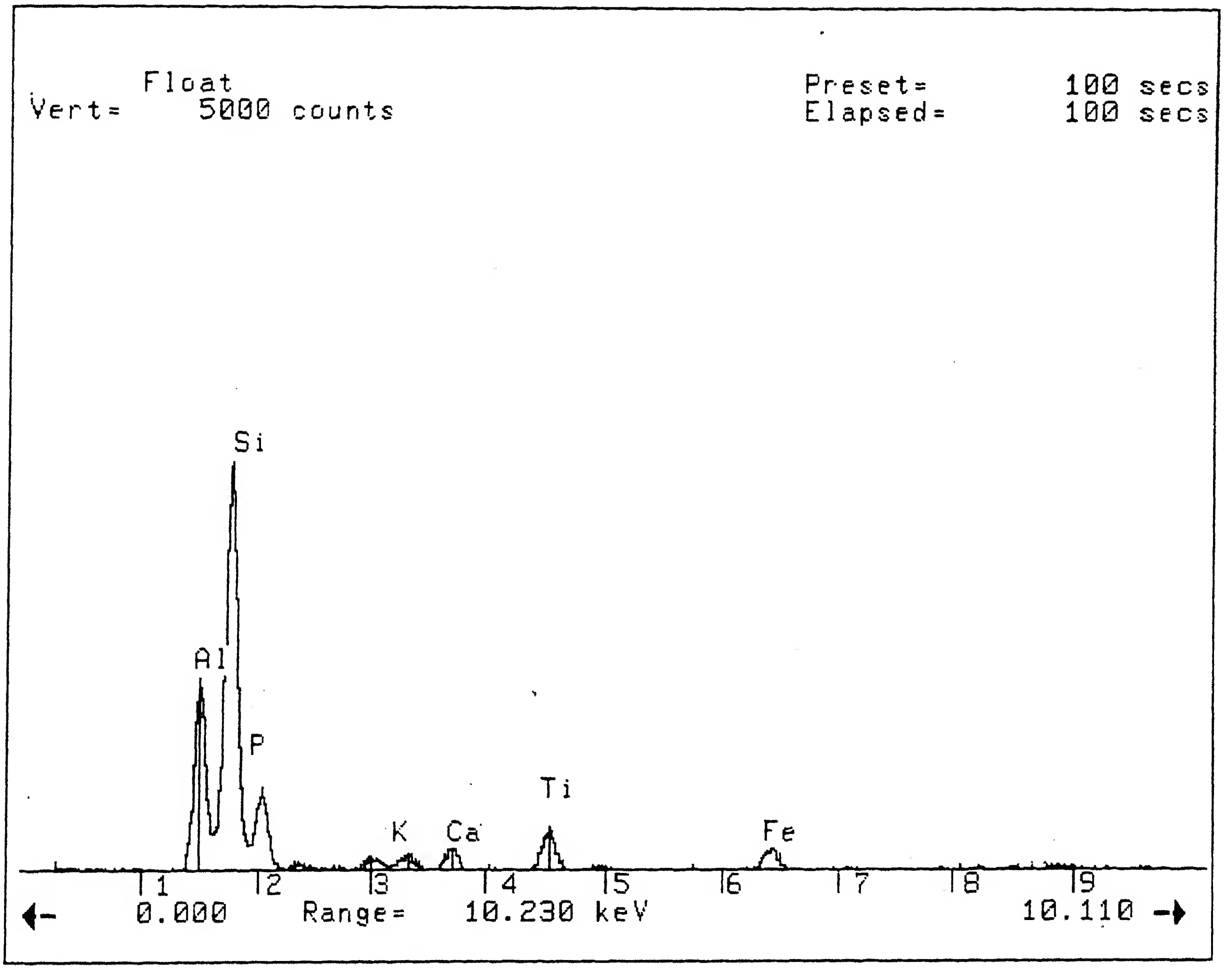


Fig-23 EDX spectra of floater of Choudwar fly ash

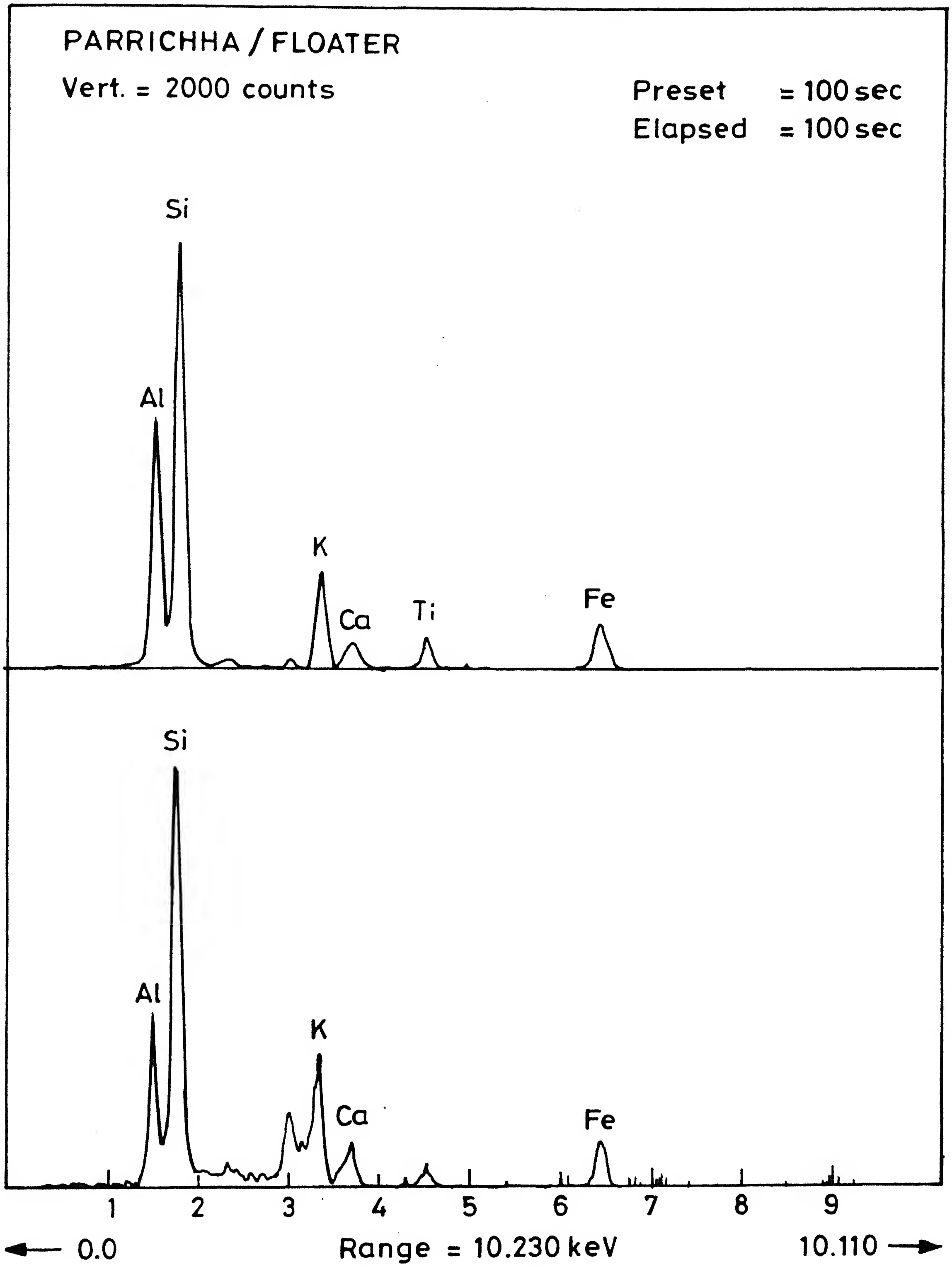


Fig-24 EDX spectra of floater of parichha fly ash

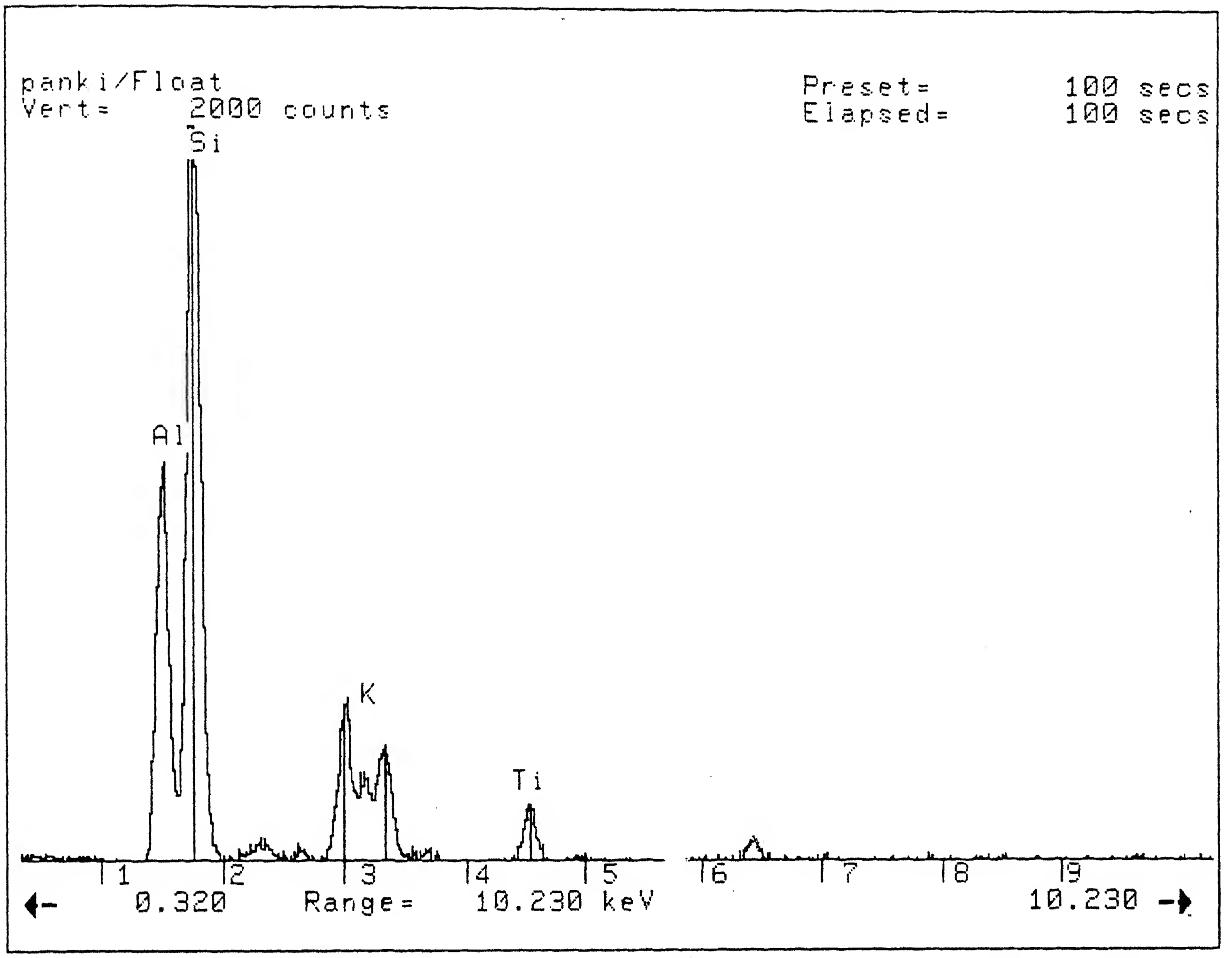


Fig-25 EDX spectra of floater of panki fly ash

ontent of a fly ash(Hubbard et al.; 1985). Higher K content of the loaters would thus indicate that the glass content of the floaters s much higher than other particles.

Collection of floaters from water suspension in case of low alcium ashes posed no problem due to the fact that free lime ontent of these fly ashes is very small(see Yudhbir and Honjo; 991) and no reaction takes place on hydration. The same is not true n case of high calcium Neyveli fly ash which contains relatively igh amount of free lime. Therefore floaters of Neyveli fly ash was ollected both from water suspension and methanol suspension. loaters collected from water suspension indicate very high content f Ca with very small amount of Al, Si, S and Fe fig-26(a). X-ray liffraction patterns of these floaters (presented later;fig-41) onfirmed Ca exists as calcite which is expected due to hydration of ree lime. Presence of needle like structure on hydration of free ime in high calcium Neyveli fly ash was observed under optical nicroscope. To doubly check this conclusion, floaters obtained from nethanol were also examined (fig-26(b)) which indicated higher proportion of Al and S compared to hydrated floaters and slightly lower content of Ca. X-ray diffraction of methanol collected floater (shown later;fig-41) indicated Ca in forms of calcium aluminate with small amount of calcite (probably due to traces of water in methanol). High sulphur content of methanol collected floaters indicate presence of anhydrite which is in the form of very tiny needles and could not be well photographed with SEM. This was also confirmed by X-ray diffraction (shown later;fig-41). Low S content

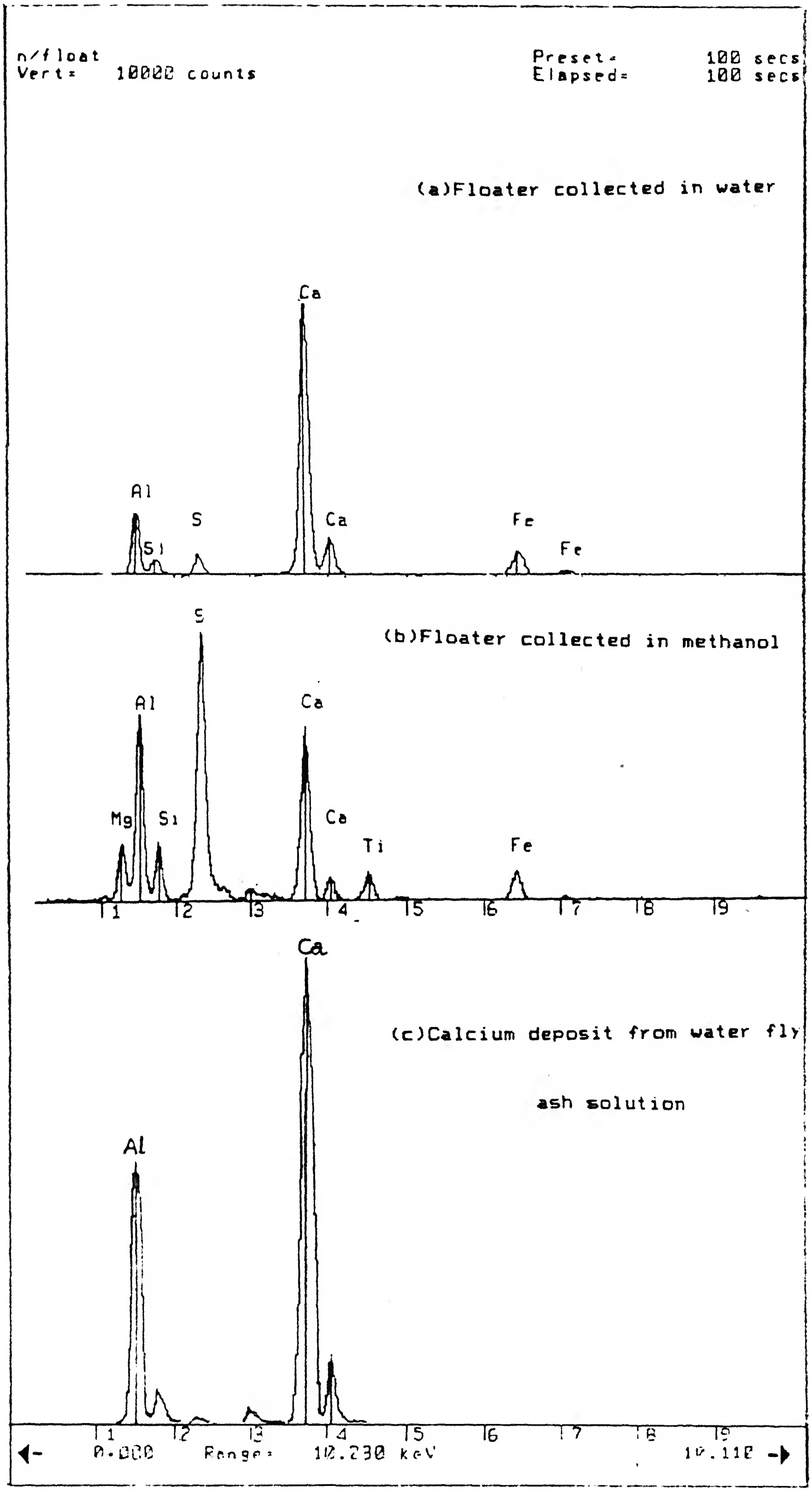


Fig-26 EDX spectra of floater of Neyveli fly ash

n hydrated floater suggests that anhydrite may have reacted with water and the product of reaction may have sedimented since floaters were collected after 24 hours of sedimentation by decantation of upper suspension. In case of methanol no reaction took place and floaters were collected by decantation of upper suspension after 1 hour.

In order to further check the presence of free lime, Neyveli fly ash was mixed with water to form a slurry and after 24 hour sedimentation, the lower suspension was put in china dish and dried in oven. Profuse coating of lime were evident on the surface as a thin skin. A small fragment, with the coating skin intact was tested for EDX analysis and the spectra is given in fig-26(c). Abundance of Ca (inform of calcite as tested by effervescence on treatment with HCl) was once again observed. Al peaks is most likely due to contamination of calcium coating with fly ash during sample preparation for EDX. Incidentally this simple method can be reliably used to check, at least qualitatively, the relative proportion of free lime in different fly ashes. Similar procedure with low calcium fly ashes produced no such coating on drying.

3.2.3 EDX spectra of individual particles

3.2.3.1 Untreated fly ash

The methanol collected floaters (fig-26(b)) had indicated high S content. In order to further check this, a small spherical floater particles of Neyveli fly as collected from methanol was tested. Fig-27 shows the spectra and confirms of very high S content which may be present as an anhydrite tiny coatings on spherical particles.

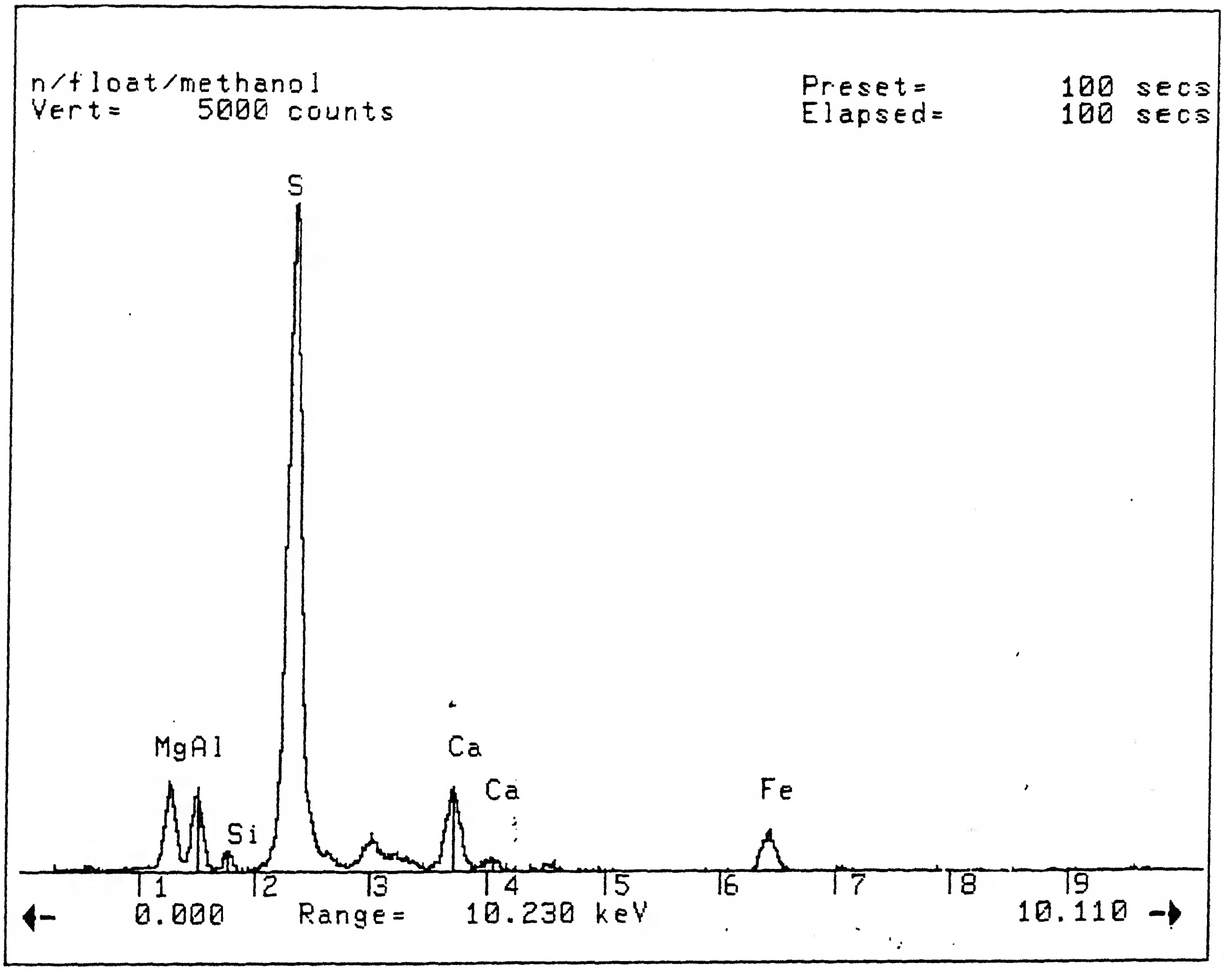


Fig-27 EDX spectra of sulphur rich Neyveli fly ash particle

Fischer and Natusch(1979) have also observed presence of anhydrite coating on fly ash particles. Incidental high Mg content suggests S may be also present as $MgSO_4$.

Fig-28 shows the EDX spectra for different fractions of Neyveli fly ash .While the coarser fraction (>75μm) is rich in Si and Fe, the fine fraction (<45μm) is rich in Ca and Al.The intermediate sizes indicate equal amount of Ca, Al and Si.

The high Si,Fe content of coarser particle is due to presence of quartz and magnetite as confirmed by optical microscopic examination(fig-5) and X-ray diffraction study (presented later; fig-39).

The very low Si content of finer grains (<45μm) was further confirmed by practical absence of quartz as seen by X-ray diffraction(fig-39). The Si may may present in some alumino silicate or calcium silicate glass phase.

It may again noted that S content increase with fineness in case of high calcium fly ash. While no difference in chemical composition are expected for different fraction of low calcium fly ashes(see Fischer and Natusch; 1979), the same was quite predominant in case of high calcium fly indicated here. The observation of Fischer and Natusch (1979) was confirmed for low calcium fly ashes and as will be discussed later, similar comments hold for mineralogical composition of different fractions.

Fig-29 to 33 depicts spectra for individual particles of Parichha and Neyveli fly ashes. For Parichha the Si,Fe and K rich particles are indicated in fig-29, 30 and 31 respectively. The SEM micrograph

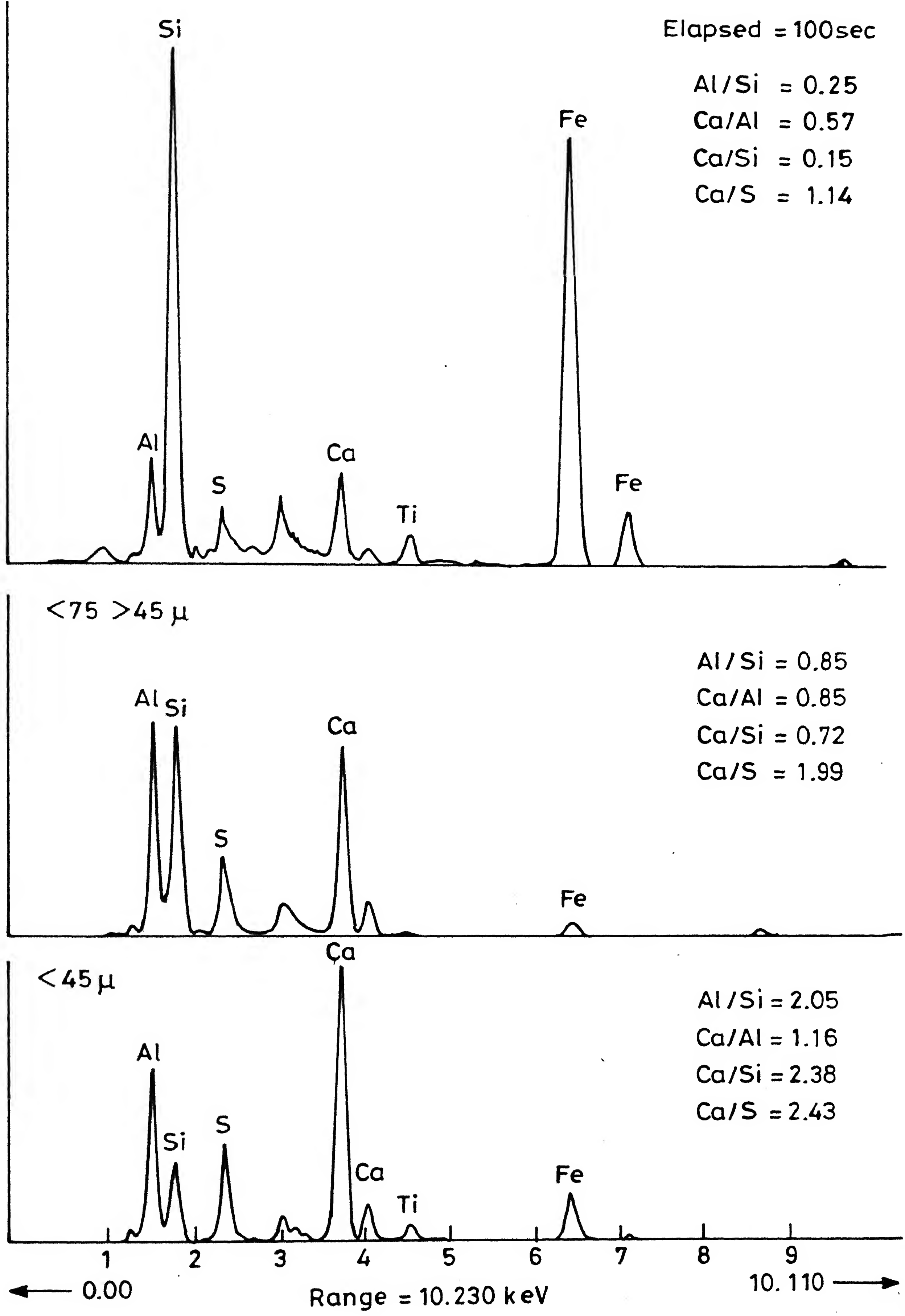


Fig-28 EDX spectra of different fraction of Neyeveli fly ash

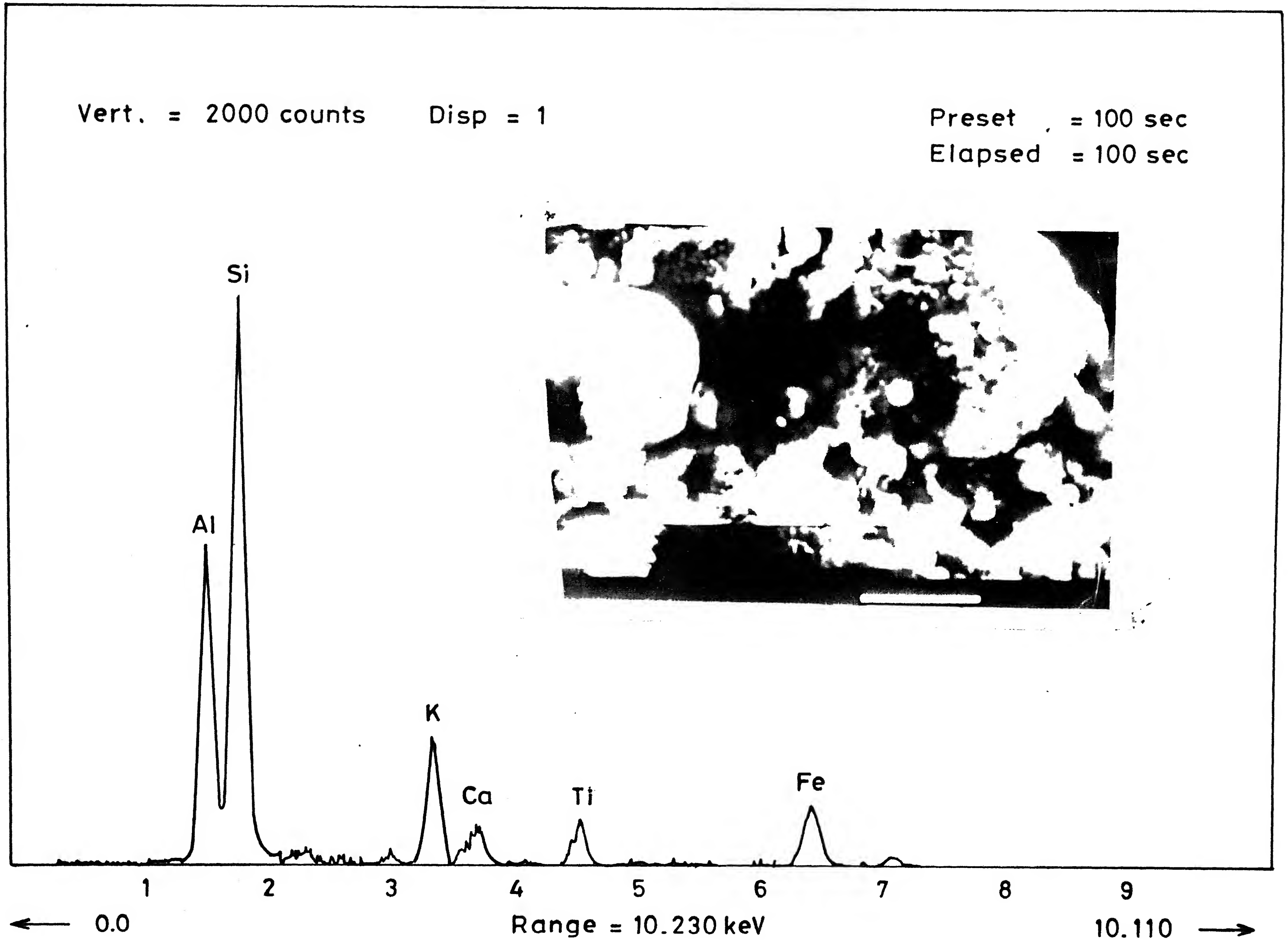


Fig-29 EDX spectra of Parichha floater

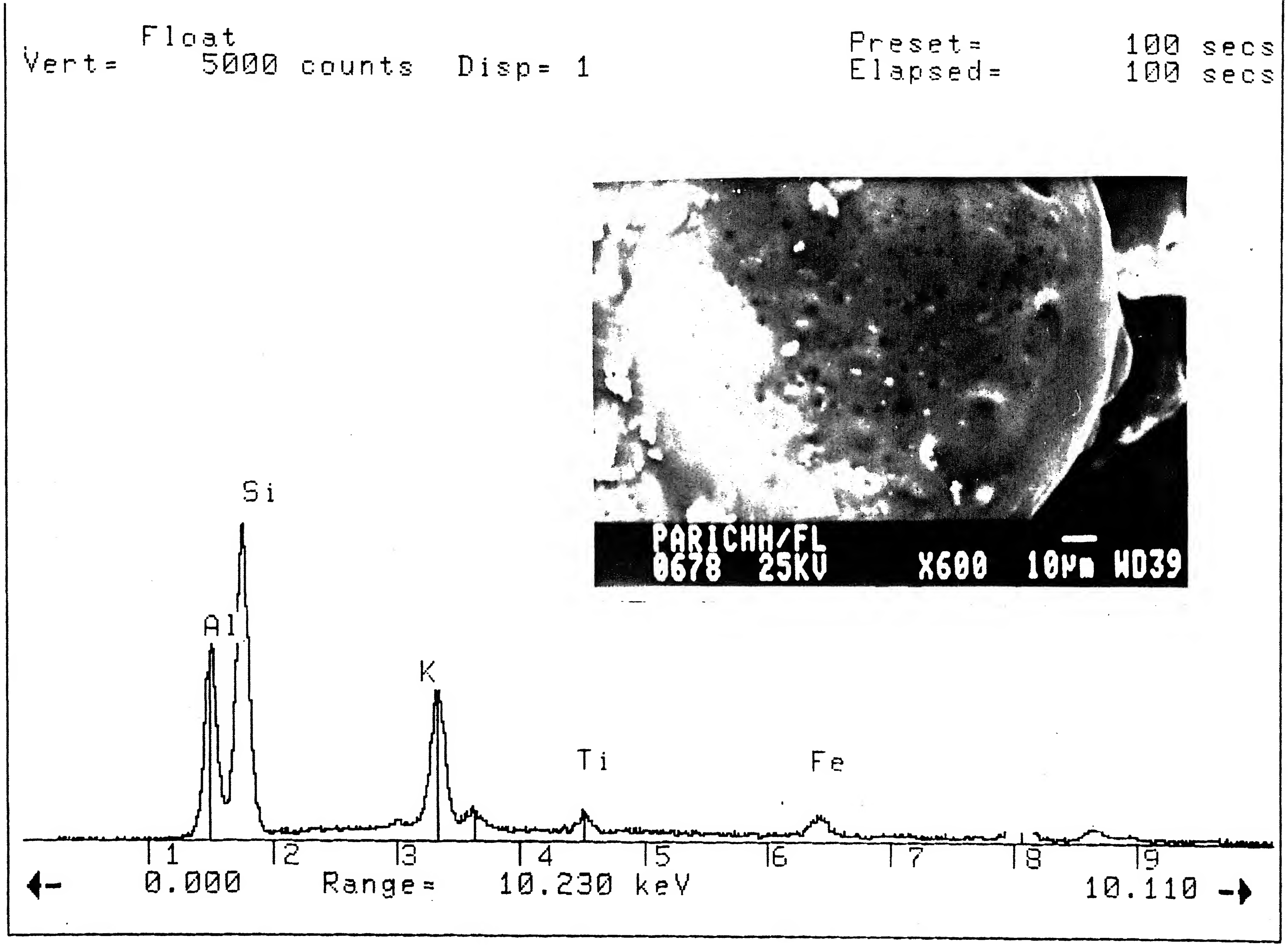


Fig-31 EDX spectra of Parichha potassium rich floater particle

of each particles is shown in the inset.

In case of Neyveli, the high Ca and high Fe particles are given in fig-32 and 33 respectively. Photographs are shown in the inset. The Fe rich particles is from the coarser fraction of the fly ash(>75μm). However some finer magnetite grains with surface coating, gave the following relative proportion of Ca,Fe and Al.

Al	4.96 %
Ca	11.00 %
Fe	81.95 %

Such a particle, after treatment with HCl (which possibly removed coatings), is indicated in fig-15(a).

3.3.2 Treated fly ash particles

Dhir et al. (1988) have suggested 2 layers of glassy material sandwiching a crystalline layer for the floater of low calcium fly ash. In this study high calcium Neyveli floater fly ash indicated 2 layers of glassy phase(see fig-17) which was further confirmed by treatment of fly ash with HCl. Fig-34 shows the alumino silicate layer after the dissolution of calcium aluminate glass outer coating. The Ag in the spectra is due to the back ground silver paint and inset shows the photograph of the particle.

Fig-35 shows the spectra for a Fe,Al rich particle of high calcium fly ash after treated with HCl. The inset shows the photomicrograph of the particle. These Fe rich portion of Neyveli would retard its reactivity.

Fig-36 depicts the EDX spectra of residual carbon with embedded small spheres (see inset photo). If we remove Ag(from

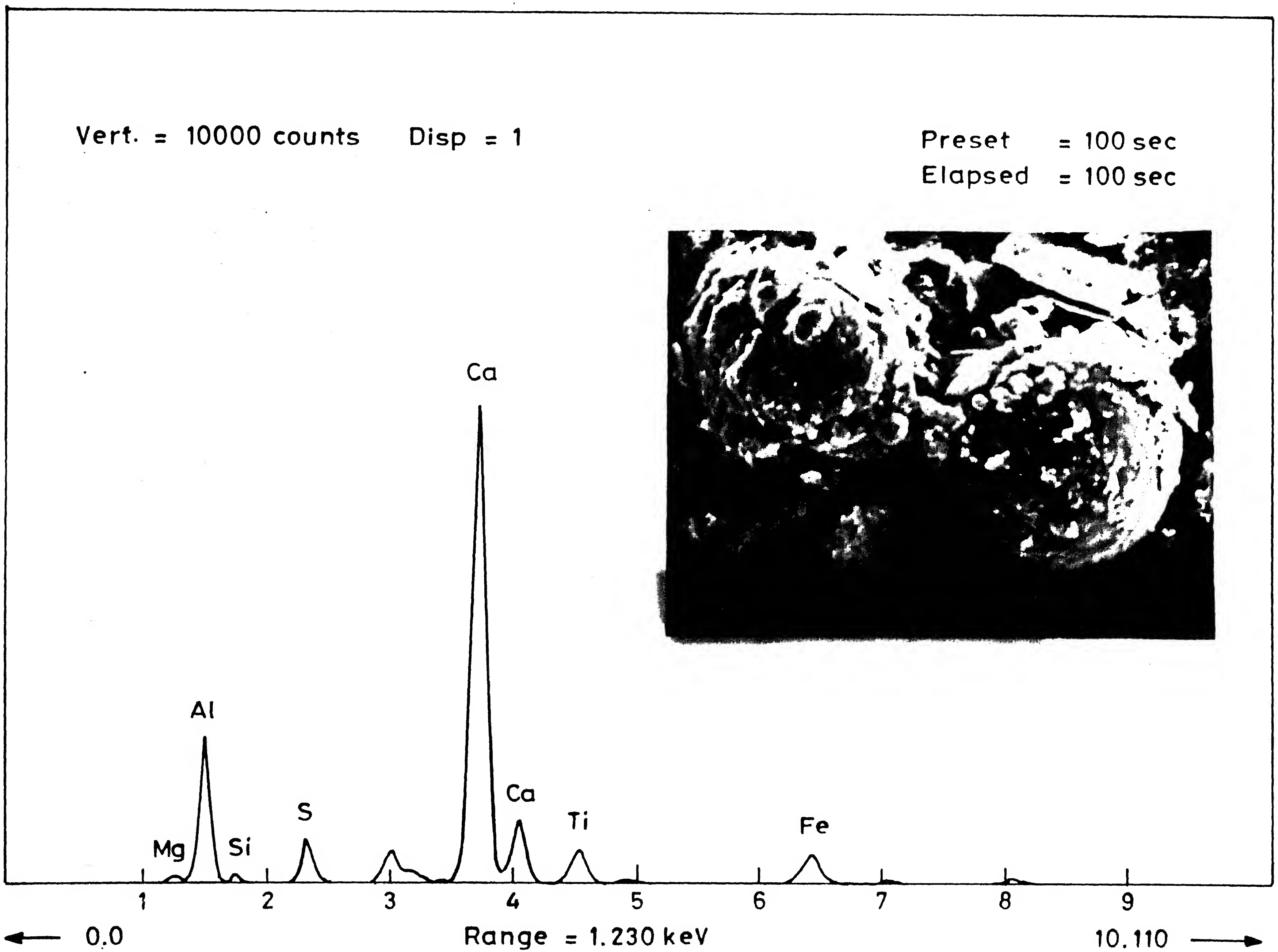


Fig-32 EDX spectra of Neyveli calcium rich particle

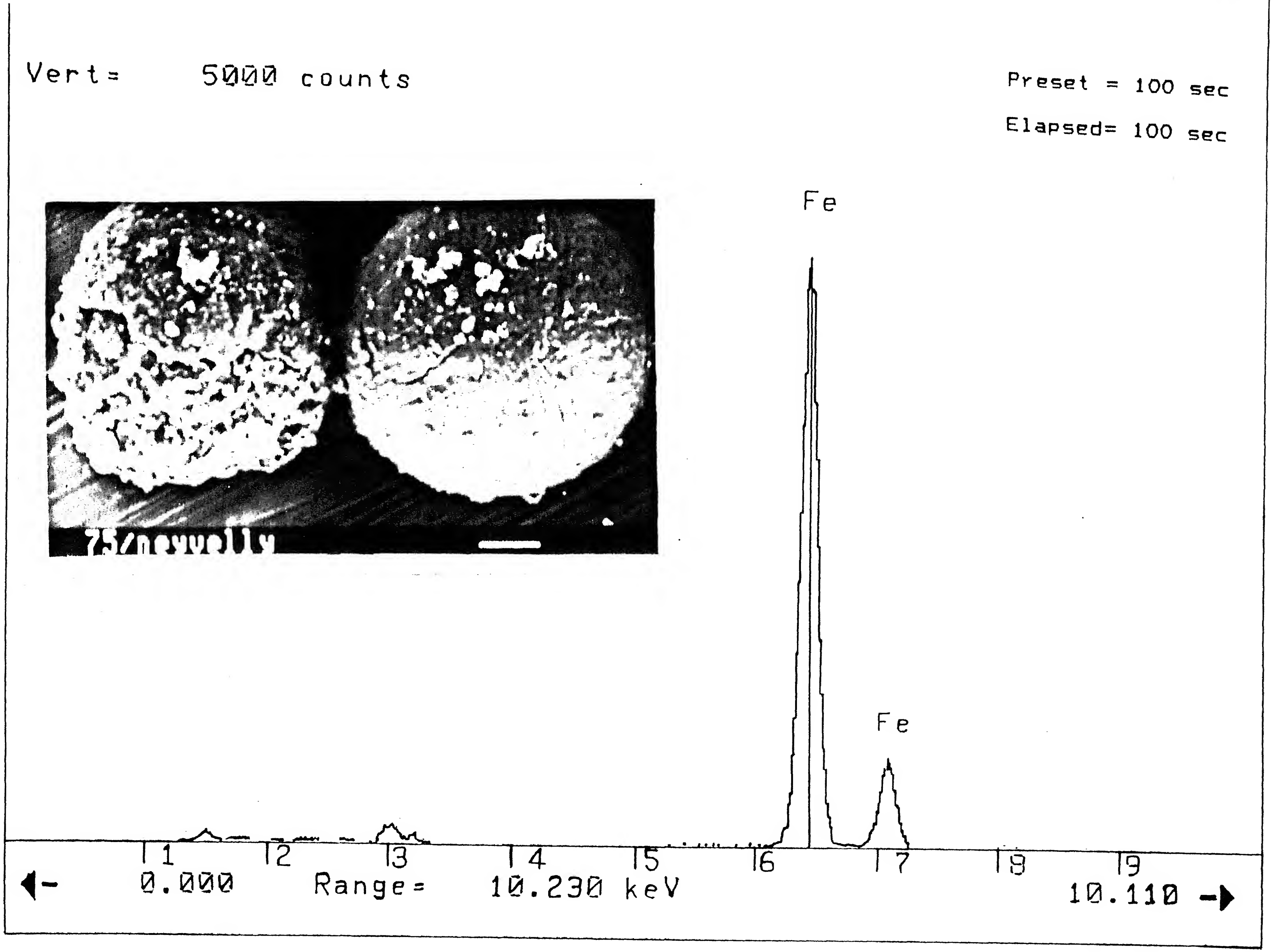


Fig-33 EDX spectra of Neyveli magnetic particle

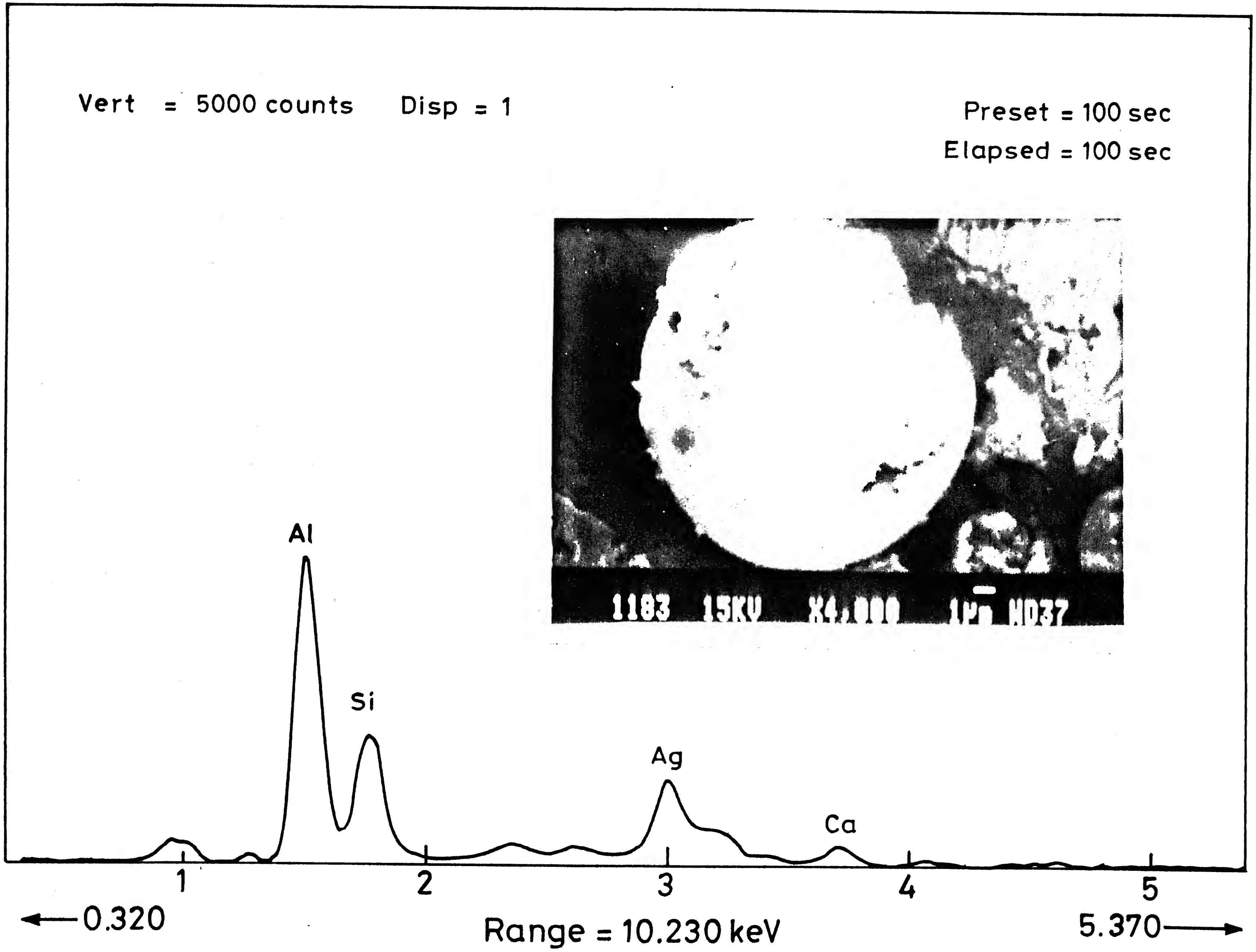


Fig-34 EDX spectra of HCl treated Neyveli fly ash

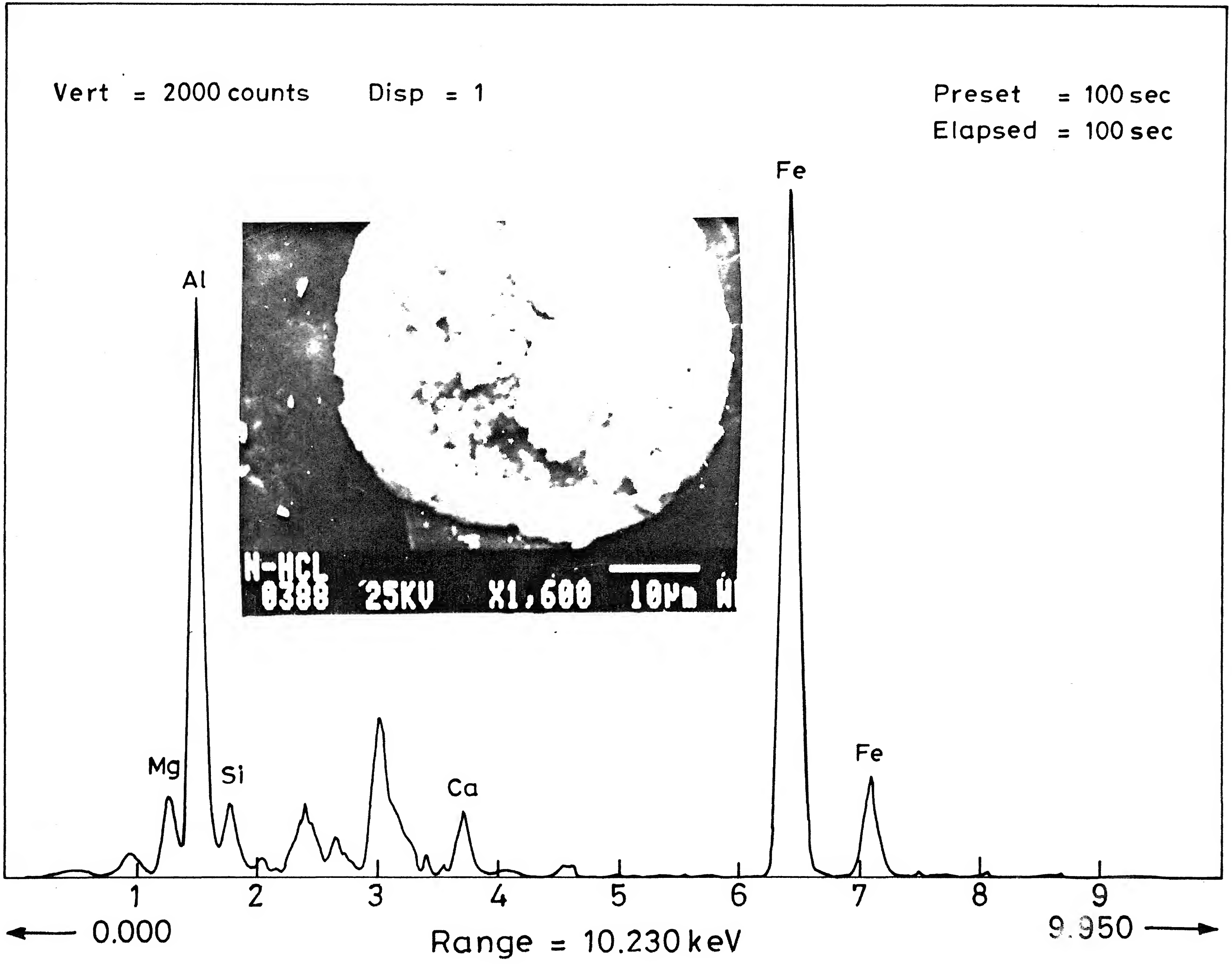


Fig-35 EDX spectra of HCl treated Neyveli fly ash

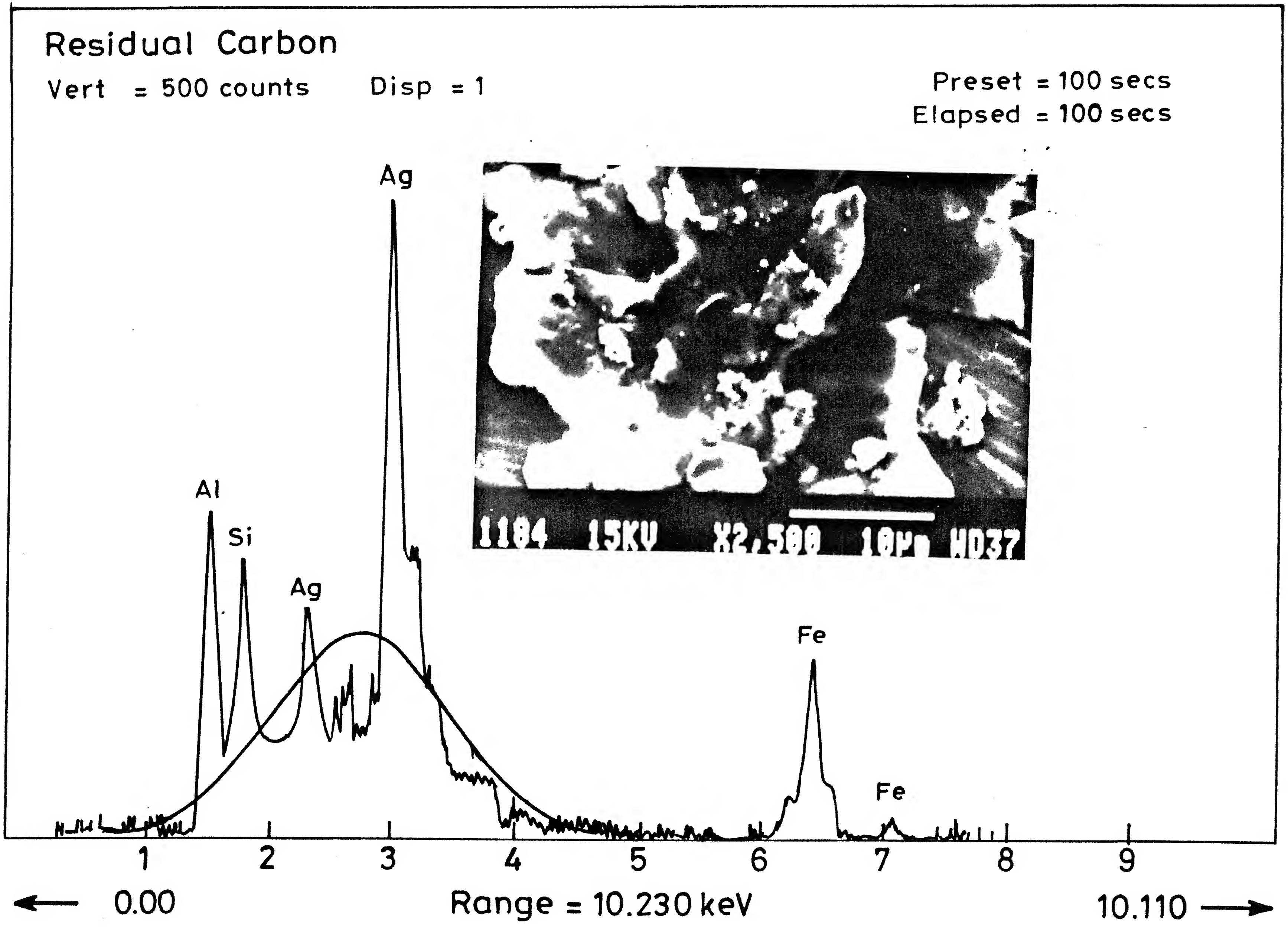


Fig-36 EDX spectra of residual carbon in Neyveli fly ash

silver paint) and Al,Si,Fe from embedded spherical particles of fly ash from the spectra, only a hump like pattern emerges as the signature obtained from a carbon particle. The actual location of carbon atom in the EDX spectra can not be located since it is outside (on left side) the energy level that had been investigated. Such a hump like background in EDX spectra is called Bremstrahlung. Fischer and Natusch(1979) suggest that class of particles indicating characteristics Bremstrahlung production are composed of elemental carbon. Thus EDX may also be used to indirectly detect the presence of carbon.

Based on these chemical investigation it may be concluded that the low calcium fly ashes are rich in Si and Al where as high calcium fly ash are rich in Ca and Al. In case of low calcium fly ash floaters contain higher K content than the total fly ash where as in case of high calcium fly ashes, the finer fraction has higher content of Mg and S compared to the whole fly ash.

As observed by Fischer and Natusch(1979) in case of low calcium fly ashes there is no difference in chemical composition between coarser and finer fraction. How ever, this is not the case for high calcium fly ash where the coarser fraction are rich in Fe and Si and the finer fractions are rich in Ca,Al,S and Mg. Thus, the coarser fraction are likely to be less reactive than the finer variety. The >75μm content may thus be good indicator of the nature of high calcium fly ash. This is not so in case of low calcium fly ash.

The low calcium fly ash and its floaters do not indicate presence of free lime where as high free lime content is observed in case of

high calcium fly ash. It is brought out that floaters in case of high calcium fly ash, should be collected from methanol suspension only since hydration of free lime in water suspension will indicate predominance of Ca.

The high calcium fly ash particles is shown to have two layers, the inner layer alumino silicate/iron layer covered by the outer calcium aluminate glass layer.

The Bremstrahlung production in EDX spectra may be used to detect carbon particles in fly ash

3.3 MINERALOGICAL CHARACTERIZATION OF FLY ASH

In addition to the chemical composition of individual particles for both the crystalline and amorphous phase of fly ash, the mineralogical composition plays a major role in determining its pozzolanic reactivity. X-ray diffraction(XRD) technique was employed to investigate the mineralogy of the whole fly ash, floater and different fraction and the results are presented in this section.

3.3.1 XRD Patterns for whole fly ash

Fig-37and 38 depicts the XRD patterns for Choudwar & Parichha and Panki & Neyveli fly ashes respectively. It will be seen that all these low calcium fly ashes are composed primarily of inert crystalline minerals such as quartz, mullite, magnetite and hematite. Comparative analysis of peaks suggests that Parichha has the highest quartz content followed by Choudwar and Panki. The mullite content in Choudwar appears to be slightly higher than that in Parichha and Panki fly ashes.

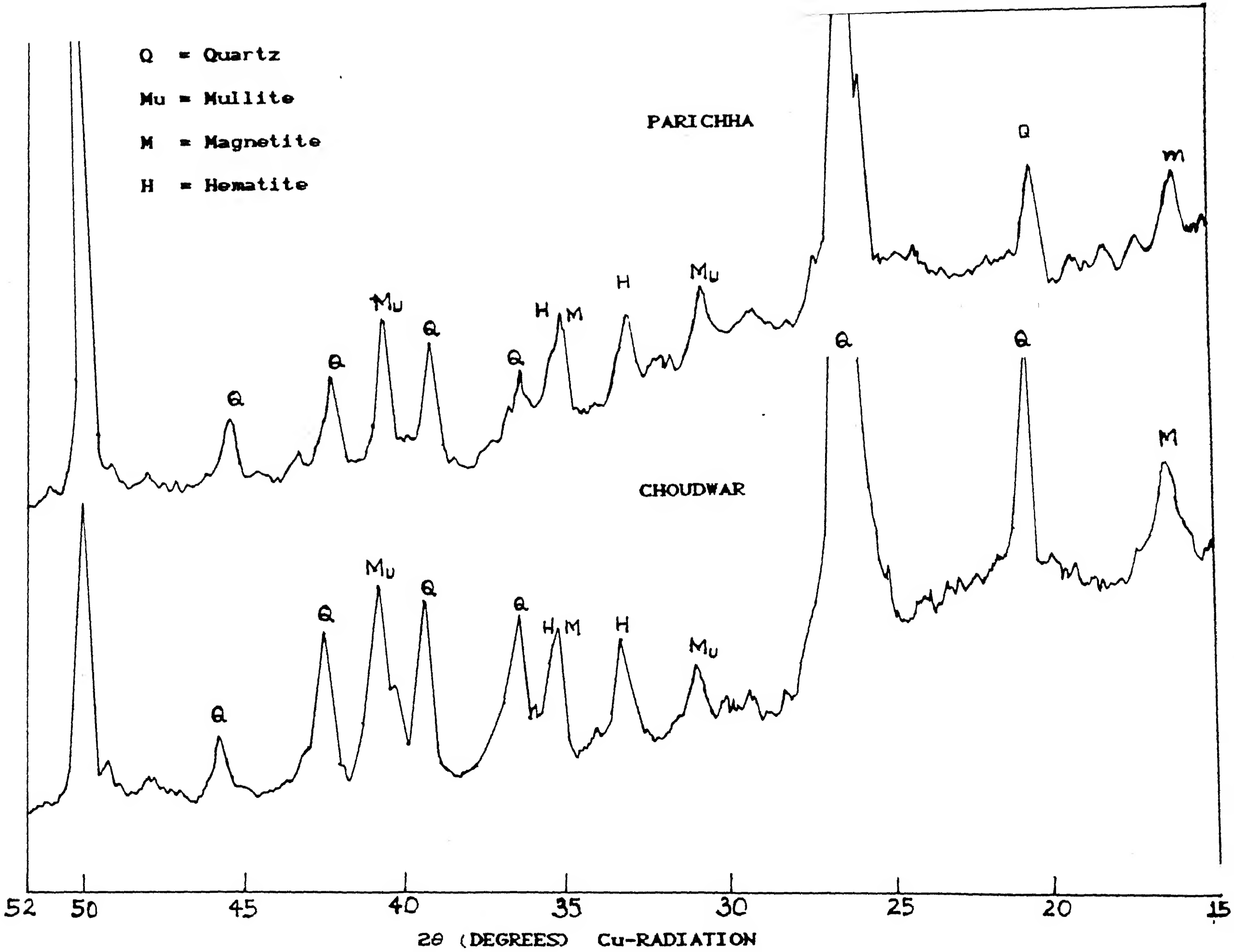
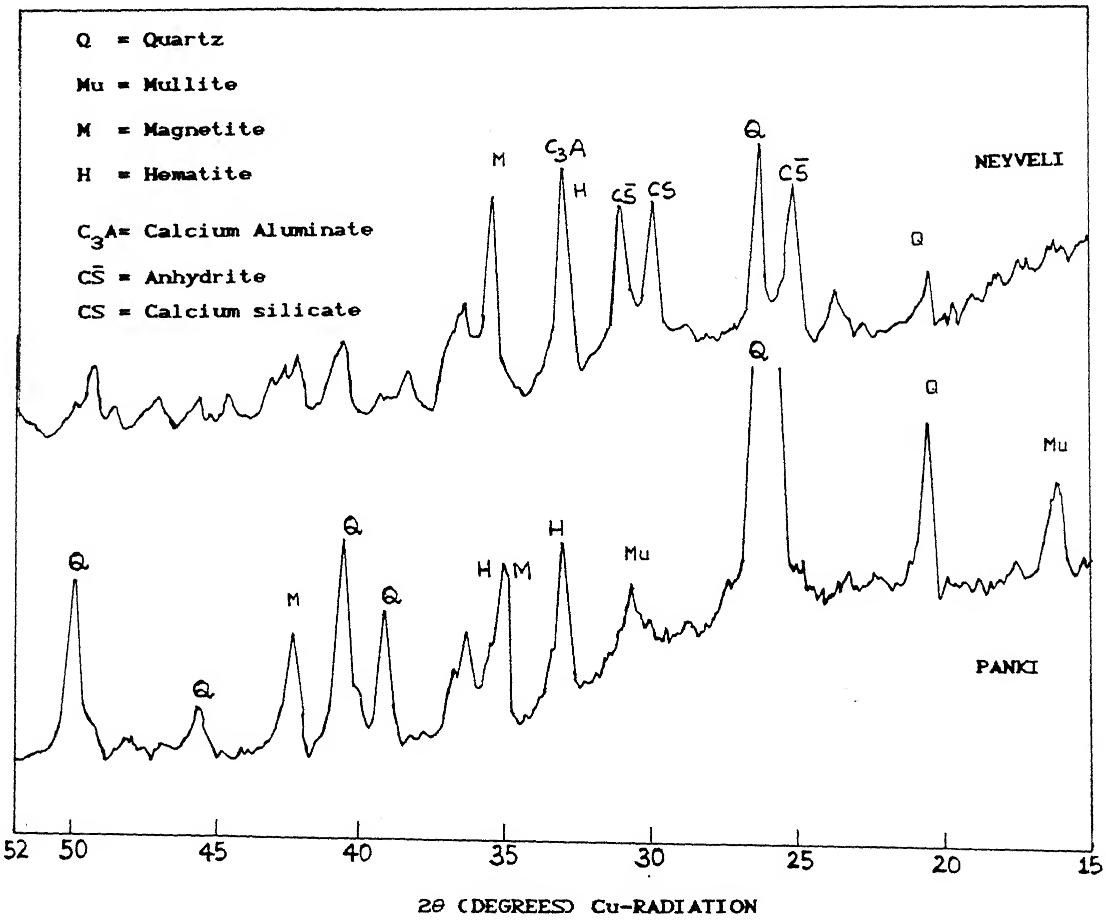


Fig-37 XRD patterns for Choudwar and Parichha fly ash



In case of high calcium Neyveli fly ash the major mineral constituents are reactive minerals such as C_3A -Calcium aluminate, CS -calcium silicate, $C\bar{S}$ -anhydrite. Mehta(1979,1985)and Lüxan et al(1989) also have reported the presence of these minerals in case of high calcium fly ash. Quartz content in Neyveli fly ash is much less compared to the low calcium fly ashes. This fly ash however has higher content of magnetite and hematite. As reported in literature, fly ash with CaO > 15 % mullite is usually absent(Mehta,1979,1985), Lüxan et al (1989)and Yudhbir and Honjo(1991). No mullite was detected for Neyveli fly ash also, which has CaO>15%.

3.3.2 XRD patterns for different fractions

As discussed in the section on chemical composition, high calcium fly ash indicate significant differences in the chemistry of the grains present in the different fractions. XRD patterns were carried out to investigate the mineralogical composition of different fraction of Neyveli fly ashes. The XRD patterns are indicated in fig-39. As will be seen, the coarser fraction(>75μm) do not contain the active crystalline minerals such as C_3A, CS, $C\bar{S}$ and are characterized by the presence of inert minerals like quartz, magnetite and hematite which are generally found in low calcium fly ashes.

In contrast to the coarser fraction, finer fraction (<45μm) is predominantly characterized by the reactive crystalline minerals and there quartz is no more present. The intermediate fraction (<75μm>45μm) exhibit mineralogical composition almost similar to the finer fraction except for the presence of high quartz content.

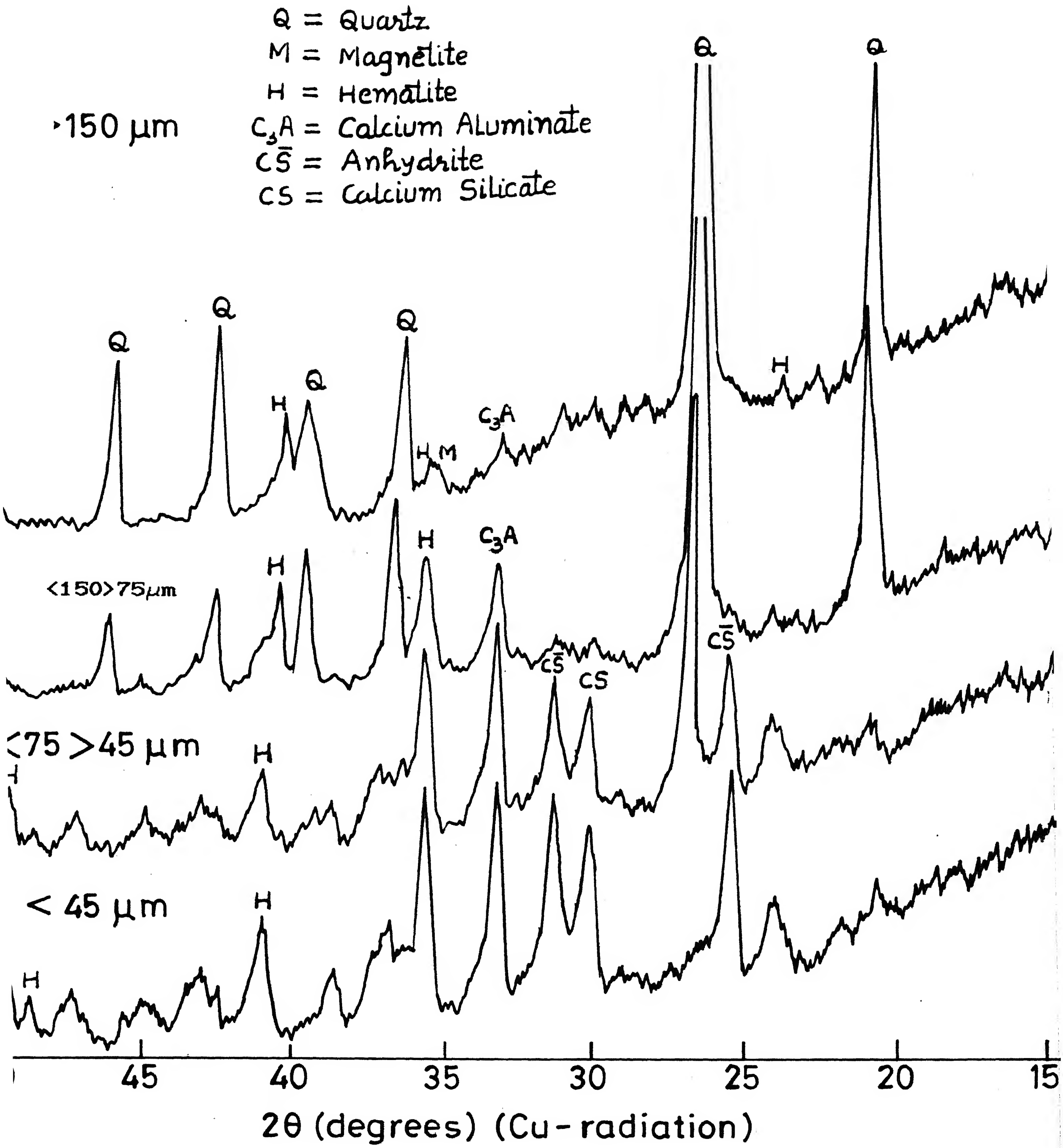


Fig-39 XRD patterns for different fraction of Neyveli fly ash

Incidentally the quartz content appears to increase with increasing particle size.(>45μm). Similarly studies were also conducted for the low calcium fly ashes but no difference was observed in mineral composition. Fischer and Natusch(1979) also make similar observation for low calcium fly ashes.

3.3.3 XRD patterns for hydrated fly ash

The presence of reactive minerals in high calcium fly ash leads to gain in strength with time on curing (some results will be presented later on) due to the change in mineralogy produced. Fig-40 present XRD patterns for hydrated Neyveli fly ash after 3, 7 and 28 days of curing. Also shown is the pattern for unhydrated fly ash for comparison. It is significant to note that with duration of hydration the amount of ettringite increases, which is known to be responsible for the gain in strength with time. The presence of ettringite in hydrated Neyveli fly ash was also observed in SEM micrograph as shown in fig-18. $C\bar{S}$ undergoes significant reduction with time and some reduction in C_3A and CS is also observed. Lüxan et al (1989) have presented similar results. Influence of hydration on high calcium fly ash is further depicted in fig-41 with a XRD pattern of hydrated floater (collected from water suspension) is contrasted with a nonhydrated floater collected from methanol suspension. Hydrated low calcium fly ashes, as to be expected, there was no change in the XRD pattern after 7 day.

3.3.4 XRD patterns to identify amorphous phase

As pointed out earlier there are mostly indirect methods which are employed to estimate the glass content in fly ash. Mehta(1979)

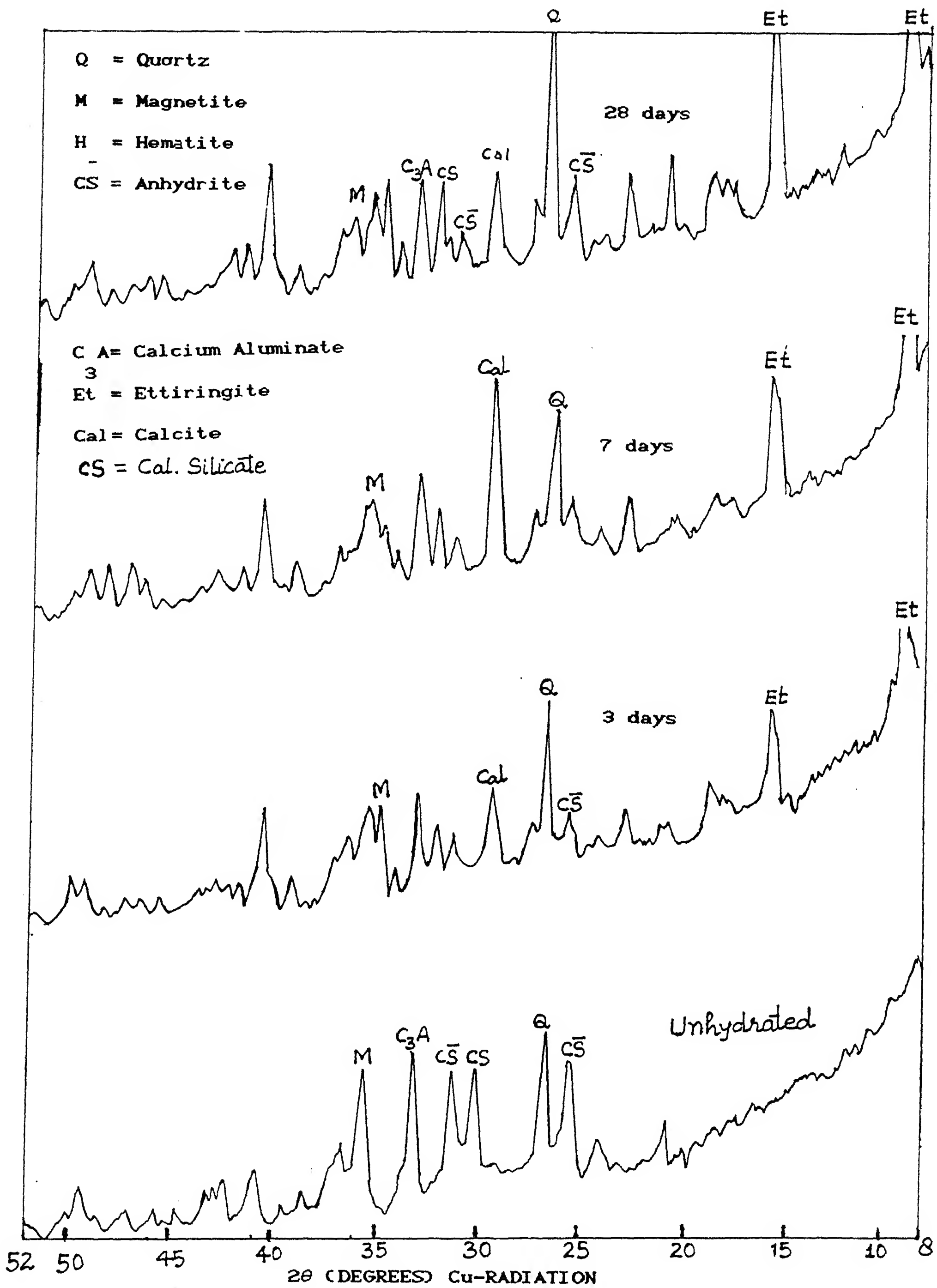


Fig-40 XRD patterns for hydrated Neyveli

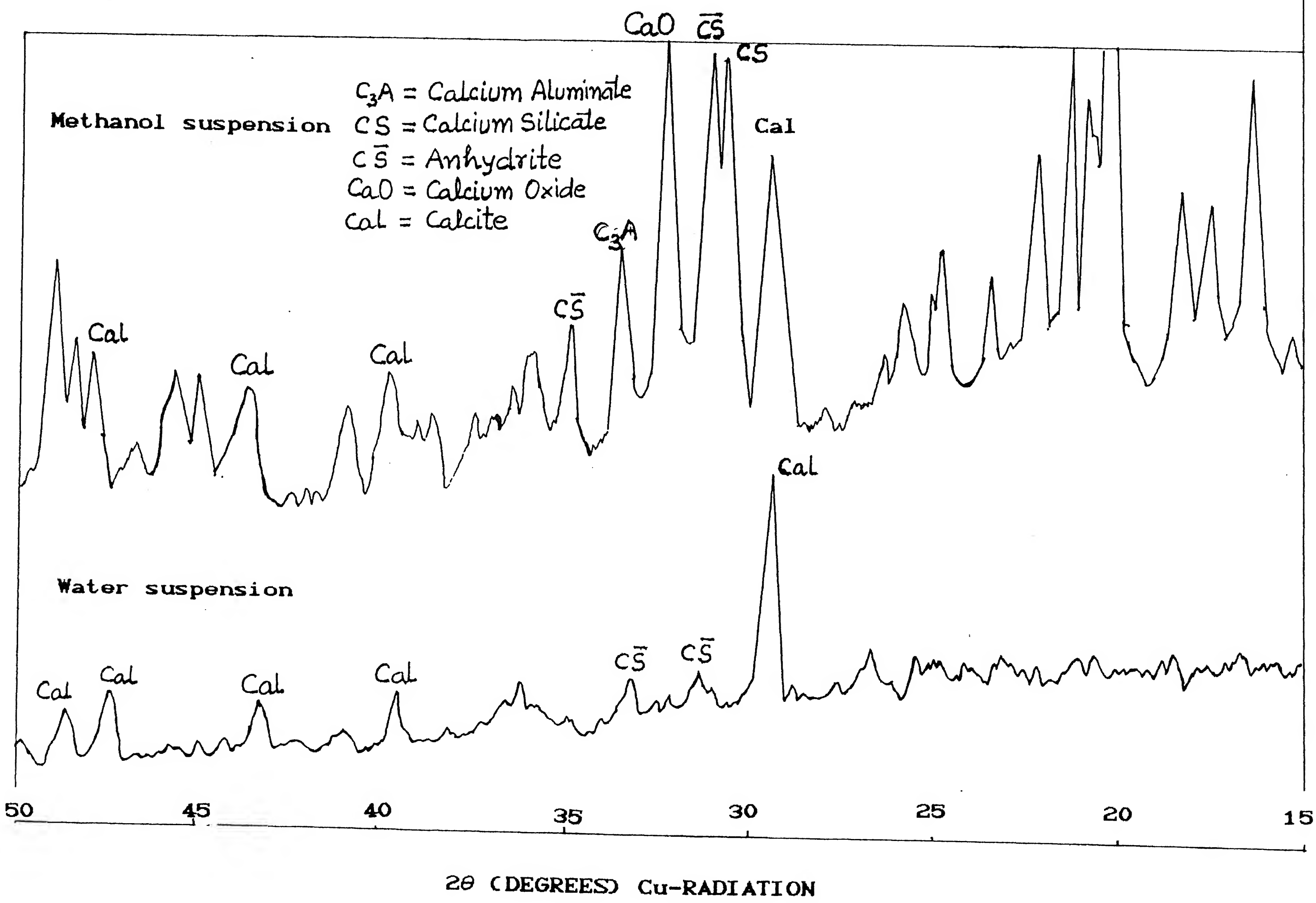


Fig-41 XRD pattern for Neyveli floater collected in water and methanol

and Diamond(1983) proposed use of XRD patterns to locate a hump (Mehta calls it diffused band) which is characteristics of the quality of the glass present. In this study XRD patterns were investigated to locate hump for four fly ashes and results were compared with the available data.

Fig-42 shows the location of humps for the four fly ashes and the results for their floaters are indicated in fig-43. The hump location for these fly ashes is compared with the results reported by Diamond(1983) as shown in fig-44. It will be seen that the results for low and high calcium fly ashes studied are comparable to the similar fly ashes investigated by Diamond(1983). While Diamond(1983) suggests 2θ value of 23-27^{o} for low calcium fly ashes, Choudwar fly ash, which has practically no analytical lime, indicates 2θ value of about 21^{o}. The 2θ values for fly ashes with analytical lime content < 20 % agree with the values suggested by Diamond(1983), however, for Neyveli fly ash which has 16 % lime content gives 2θ value of 28^{o}for whole fly and a 2θ value of 32^{o} for its floater which was found to be composed of calcium aluminate as brought out by by EDX spectra shown in fig-26(b). The floaters of low calcium Choudwar, Parichha and Panki fly ashes, however, indicated 2θ values of about 26^{o}.

Diamond(1983) presented a relationship between 2θ value of hump position and amount of analytical lime content. Fig-45 shows available data, for low and high calcium fly ashes. The results for whole fly ash and their floaters for Choudwar, Parichha, Panki and Neyveli are also indicated. Further more data for Panki fly ash

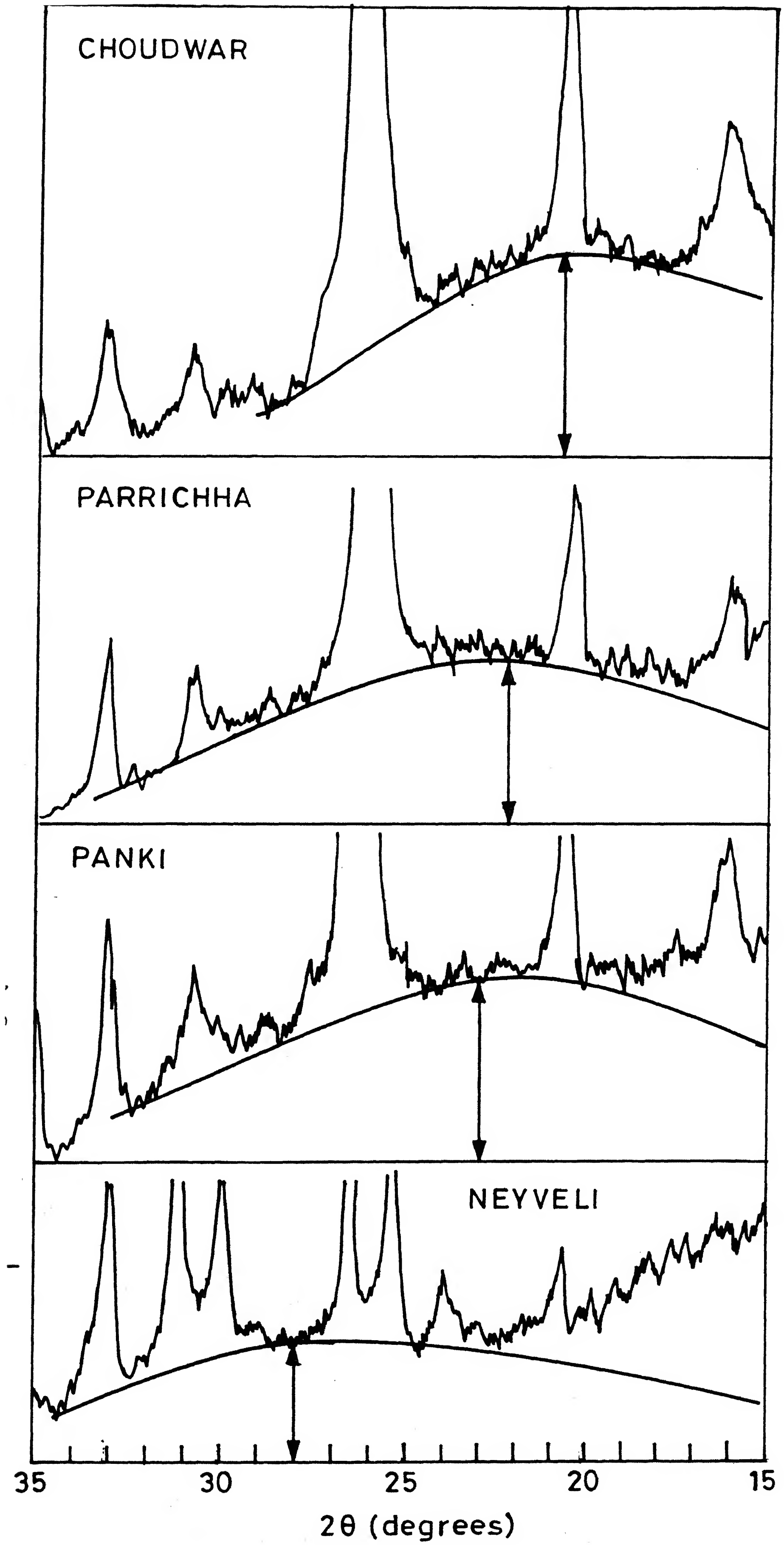


Fig-42 XRD patterns for Choudwar,Parichha,Panki and

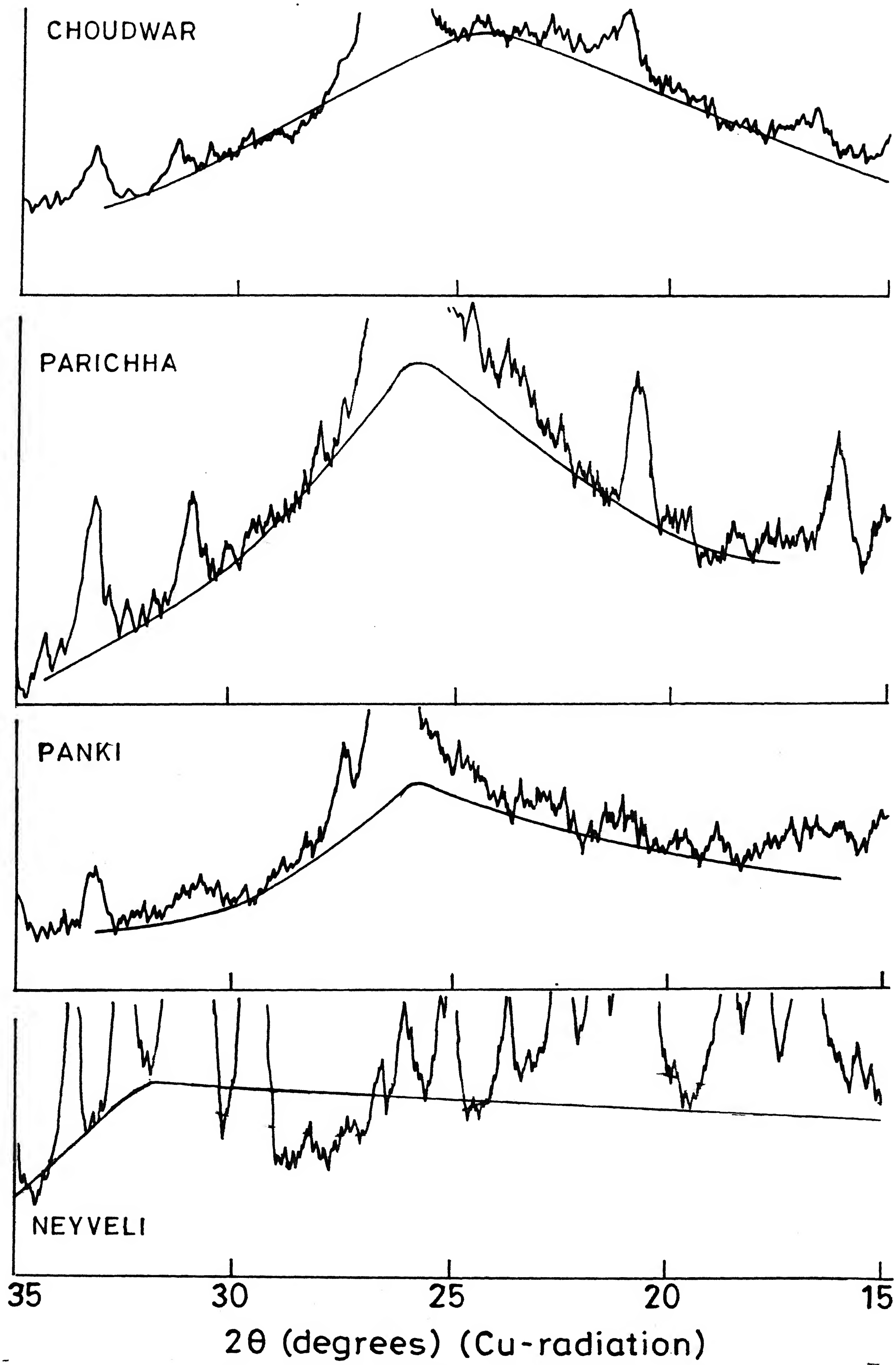


Fig-43 XRD patterns showing hump position for floater of choudwar

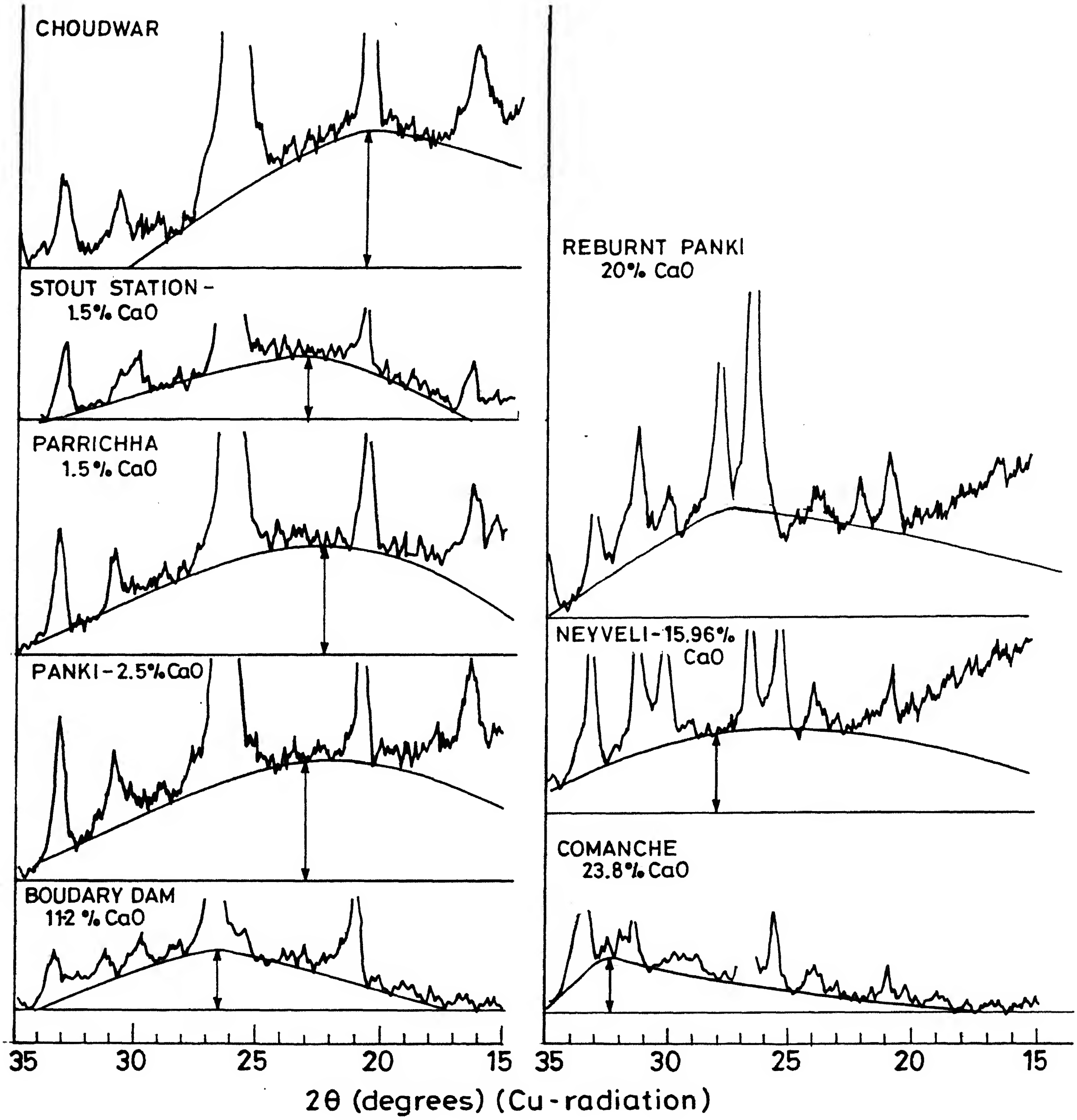


Fig-44 comparative study of hump position for different fly ashes

samples, mixed with 10 % and 20 % lime burnt in the furnace at temperature ≥ 1100 °C and cooled subsequently, are also presented in fig-45. The hump location for 20 % lime treated fly ash is shown in fig-44.

The shift in hump position from 22° ($\simeq$ 0% lime) to 28° (~ 20 % lime) appears to indicate the changes in the type of glass present. The sudden jump from 2θ = 28° to 2θ = 32° once again is indicative of the major change in the quality of glass present.

Samples of Parichha and Panki represent lime content of 1.5 and 2.5 % respectively and the 2θ (hump position) value is indicative of predominantly alumino-silicate glass where as in Choudwar with practically no lime, appears to be of siliceous type. The floaters of these fly ashes, however, indicate alumino-silicate glass type. In case of Panki addition of lime has increased the 2θ and at 20 %. lime content the glass is predominantly of calcium-alumino-silicate variety.

The Neyveli fly ash as a whole also appears to contain predominantly Calcium - Alumino-Silicate type glass, however, the floaters appears to be composed of calcium-aluminate type glass giving hump position at 32° 2θ. Evidence of the presence of calcium aluminate and alumino-silicate glass in Neyveli was presented in form of EDX spectra shown in fig-32 and 34 respectively.

It may be pointed out that while the hump location should be identified with a particular peak position, the presence of mixture of different glass type will cause interference and determine the actual location of the hump for a given fly ash. The 22°, 26°,

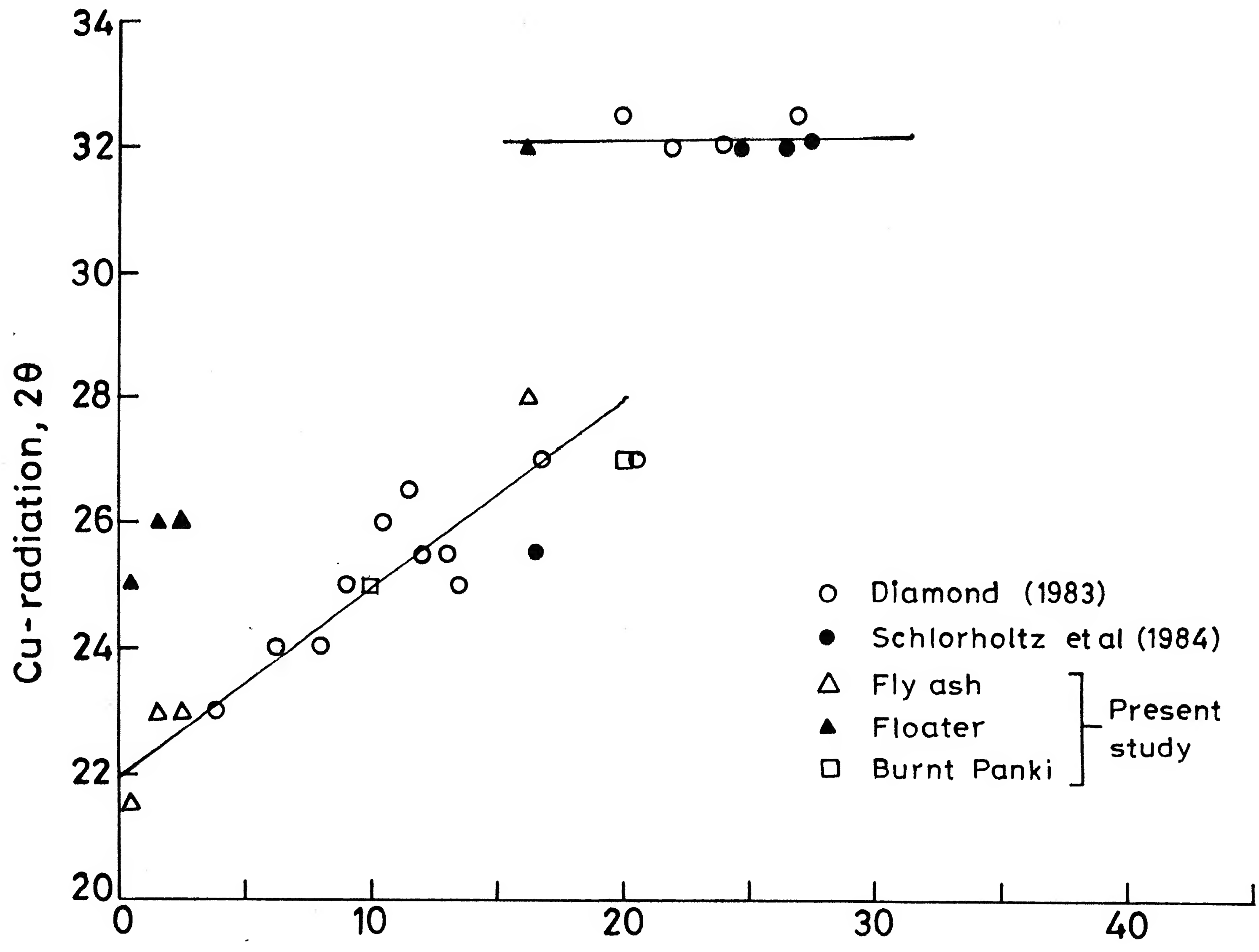


Fig-45 Relationship between hump position and anlytical lime

28° and 32° hump position are however indicative of the predominantly siliceous, alumino-silicate, calcium-aluminum -silicate and calcium aluminate glass respectively. Incidentally for lime content greater than 15 to 20% the CS minerals is found in fly ashes. For Panki fly ash, quartz content decreased considerably as the fly ash(original lime content of 2.5 %) was burnt with 20% lime at temperature $\geq$ 1100° C and the XRD pattern indicated CS peak in the burnt fly ash, which was not there in the original sample. Yudhbir and Singh(1991) on the basis of gross chemical content (normalized for carbon content), have reported decrease in SiO_2 content with increase in lime beyond 15-20%. This may be due the use of SiO_2 in the formation of CS mineral.

It is well appreciated that both the amount and quality of glass present are important in determining the pozzolanic reactivity of fly ash, especially low calcium variety. while the 2θ (hump position) analytical lime content relationship helps to asses the quality of glass present, the amount of glass content should also be known. As indicated in the review chapter, there are basically two methods; direct and indirect to asses the amount of glass present. Here we will present the indirect method, based on the results of chemical analysis, to estimate the glass content.

Fig-46 presents available data for low calcium fly ashes in terms of glass content vs ratio of K_2O and Al_2O_3. The details of these data points are presented in Table-4. The data suggest a good correlation and would indicate higher glass content for fly ashes with higher K_2O as Al_2O_3 does not vary significantly for these fly

TABLE 4

Data for K/A vs. glass content relationship

			K/A	GLASS CONTENT	CaO	SOURCE
S.W.	1	P13	1.10	62	1.9	
	2	P14	1.11	65	3.9	
S.E.	3	p15	0.91	50	3.0	
	4	P16	0.70	43	2.5	
	5	P17	0.68	52	2.8	
M.D.	6	P18	1.19	67	2.4	
	7	P19	0.90	55	5.5	
	8	P20	0.78	63	3.5	
	9	P21	1.15	66	2.3	
	10	P22	1.00	53	7.4	
	11	P23	0.78	63	7.6	
	12	P24	1.18	62	1.9	
N.W.	13	P25	1.17	70	3.0	
N.E.	14	P26	0.78	45	3.0	Hubbard et al. (1985)
	15	P27	1.20	70	1.6	
	16	P28	1.17	70	1.4	
	17	P29	1.16	64	1.2	
	18	P30	1.32	62	2.0	
Scot	19	P31	0.30	40	2.8	
	20	P32	0.40	29	3.8	
P.L.	21	P33	0.81	48	2.4	
	22	P28/P	1.17	72	1.4	
	23	P25/P	1.21	73	3.6	
	24	P20/p	0.86	74	3.1	
	25	P31/P	0.41	45	3.2	
	26	P24/P	1.14	67	1.6	

27	Fiddler's Ferry	1.48	80	3.39	Halse et al. (198
28	West Burton	1.45	81.5	1.67	
29	Nanticoke	0.48	54	5.95	Van Roode et al. (1987)
30	Lakeview	0.77	55.6	3.82	
31	Lingan	1.59	77.3	1.29	
32	Dalhousie	1.44	76.7	4.45	
33	Dunston(i)	0.98	77	2.10	Watt and Thorne (1965)
34	Dunston(ii)	0.6	80	1.70	
35	Ferry Bridge(i)	1.62	86	2.40	
36	Ferry Bridge(ii)	1.57	88	2.10	
37	Hams Hall	1.2	83	3.40	
38	Rye House	0.96	71	7.70	
39	Skelton Grage	1.54	79	3.40	
40	A1	1.0	73	1.81	Valent et al. (1988)
41	A2	1.0	75	1.89	
43	P1	1.15	67	7.22	
44	P2	0.83	63	6.34	
45	Akichi	1.11	57.8	7.30	Yudhbir & Honjo (1991)
46	Japan	0.45	56.2	6.30	
47	Wit Bank	0.89	49.0	2.9	
48	Milla blend	0.47	54.4	5.6	
49	Tengi	0.43	29.3	5.2	
50	Ermelo	0.13	42.5	8.1	
51	Tengi	0.42	35.2	5.0	
52	Moura Wamko	0.72	60.1	2.4	
53	*****	0.14	37.1	8.5	
54	Ermelo	0.16	41.0	7.9	
55	Wit Bank+Tengi	0.27	30.5	9.0	
56	Milla Blend	0.84	47.3	2.9	
57	WitBank + Tengi	0.29	40.7	6.9	
58	WitBank	0.10	35.3	10.0	
59	Milla Blend	0.84	56.5	2.9	

60	Ermelo	0.19	39.2	8.5
61	Tengi	0.43	42.4	4.5
62	Ermelo+Tengi	0.30	29.0	5.7
63	Tengi	0.42	35.4	4.6
64	Milla Blend	0.89	54.5	2.9
65	WitBank +Tengi	0.21	40.3	7.2
66	Ermelo	0.18	36.5	8.3
67	Ermelo+Tengi	0.30	34.4	5.7
68	WitBank	0.09	33.4	10.1

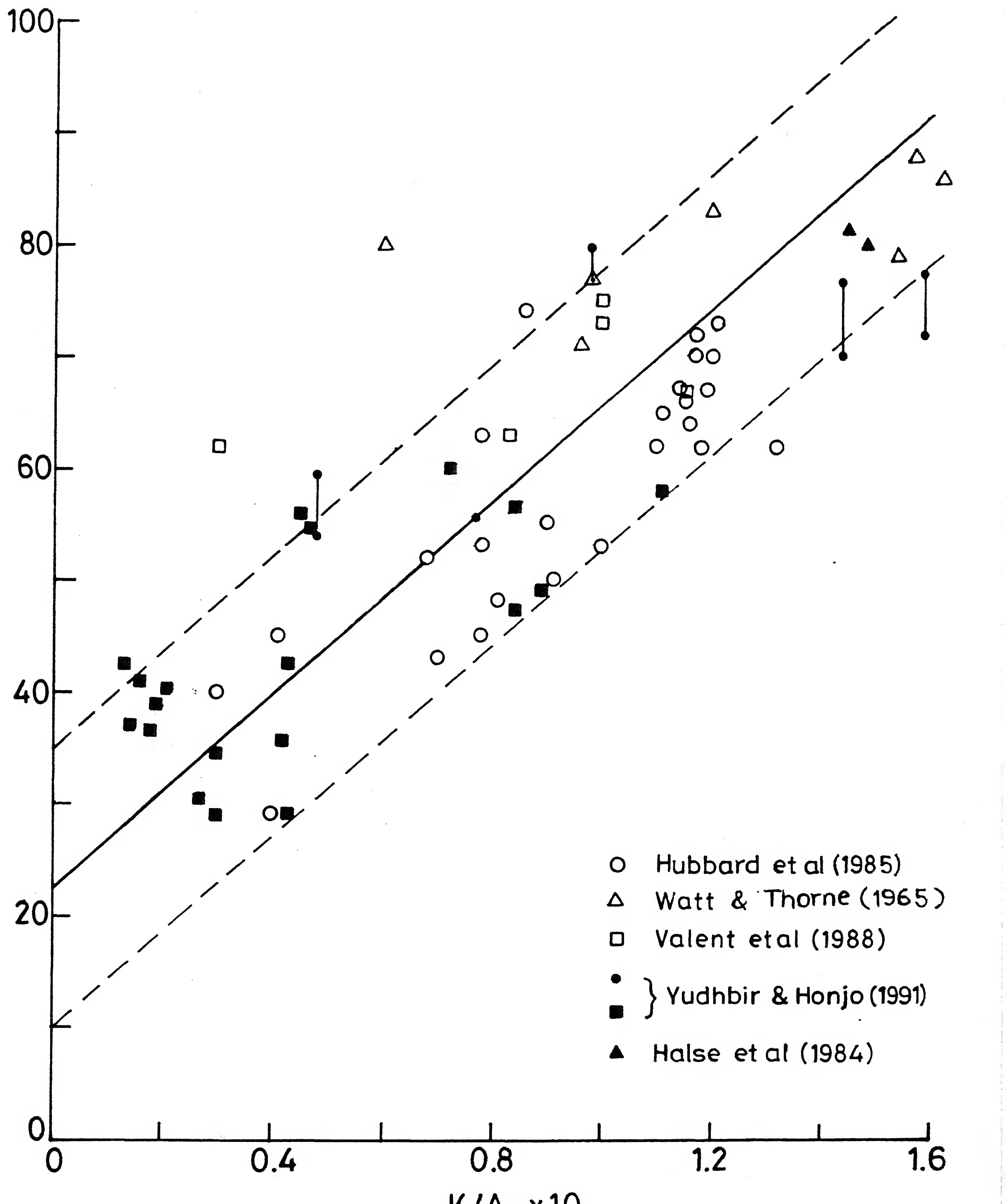


Fig-46 Relationship between glass content and K/A ratio

ashes.(see Yudhbir and Singh ; 1991).

It is interesting to observe that for these low calcium Indian fly ashes, the estimated glass content from fig-46 lies below 50 % and as shown in fig-45 the quality of this glass varies from siliceous to alumino silicate type only. This may help to explain the low reactivity of these fly ashes with lime (see Singh;1989). A detailed discussion on this respect will be given under section on gain in strength with addition of lime. As it is well known that the floaters are primarily made of glassy material (Hubbard et al ;1985), the higher K content in floaters of Parichha and Panki (as indicated earlier fig-24 and 25 respectively) compared to whole fly ash, would support the increase in glass content with higher K_2O relationship depicted in fig-46.

It would thus appears encouraging to recommend the relationship shown in fig-46 to estimate the glass content within ±12 % tolerance on the basis of K/A ratio which can be calculated from the gross chemical analysis usually reported for all fly ashes. The determination of the quality of glass however, would need XRD pattern which again is not very difficult to obtain.

On the basis of these results it may be concluded that the low calcium fly ashes contain primarily inert crystalline minerals such as quartz, mullite, hematite and magnetite and the mineralogical composition of different fraction of these fly ashes is invariant.

In case of high calcium fly ashes, the major mineral constituent are quartz, hematite, magnetite (inert type) and C_3A, CS, $C\bar{S}$ (reactive type). The coarser (>75 μm) fractions contain quartz,

hematite and magnetite where as the finer fractions (<45μm) contain C_3A,CS, C$\bar{S}$ and magnetite. No quartz is present in this fraction.

The high calcium fly ash on hydration indicates the formation of ettringite which is responsible for gain in strength with time. No such change in mineral composition was observed in low calcium fly ashes.(This is to be expected).

Based on the XRD pattern and the location of hump(2θ), which is indicative of the quality of glass present, a 2θ vs analytical lime content relation is useful for evaluation of the quality of glass as suggested by Diamond(1983).

On the gross chemical analysis the K/A ratio suggested to evaluate the amount of glass content in low calcium fly ashes. This relationship was originally suggested by Hubbard et al (1985). The data on high K content of glassy floaters presented here further validates this relationship.

3.4 SOME ENGINEERING PROPERTIES

Use of fly ash as a geotechnical construction material for embankment or reclamation fills would require evaluation of their engineering properties. In this study only the grain size, compressibility, compaction, unconfined stress-strain and gain in strength with time of compacted fly ashes were studied. The results are presented here and comparison are made with the values reported in literature.

3.4.1 Grain size

In fig-2 the general range of variation in grain size distribution for a wide range of fly ashes was reported. The result

of normally used hydrometer analysis for the four fly ashes are now compared with the Coulter Counter procedure.

As discussed earlier the low calcium fly ashes do not undergo any significant changes in chemical composition on hydration, one would not expect any difficulty in using hydrometer method for grain size studies. How ever, for high calcium fly ash, hydration produces significant chemical changes as free lime react with water (see Koo; 1991). Therefore for high calcium fly ashes either grain counting by optical microscope (Koo; 1991) or electrolyte resistivity (Coulter Counter) method (Valent et al.; 1988) have been suggested for grain size distribution. Fig-47 shows data by Coulter Counter method and the comparison with hydrometer analysis is indicated in fig-48. As will be noted, for Parichha and Panki, the difference between the two methods are rather smaller, where as in case of Neyveli high calcium fly ash, hydrometer underestimates the <45μm fraction. It would thus seen important that Coulter Counter method be used for grain size distribution analysis of high calcium fly ashes.

3.4.2 Compressibility

Fig-49 shows results of oedometer test on two fly ashes. The objective of this limited study was only to emphasize the fact that while for low calcium fly ashes like Panki, conventional oedometer test can be used, it is not possible to investigate compressibility of high calcium fly ashes by the same procedure. This is due to the fact that these fly ashes (as discussed later) shows very high self hardening behavior when mixed with water and compacted. The fly ash sample become almost rock like in the oedometer as shown in fig-49.

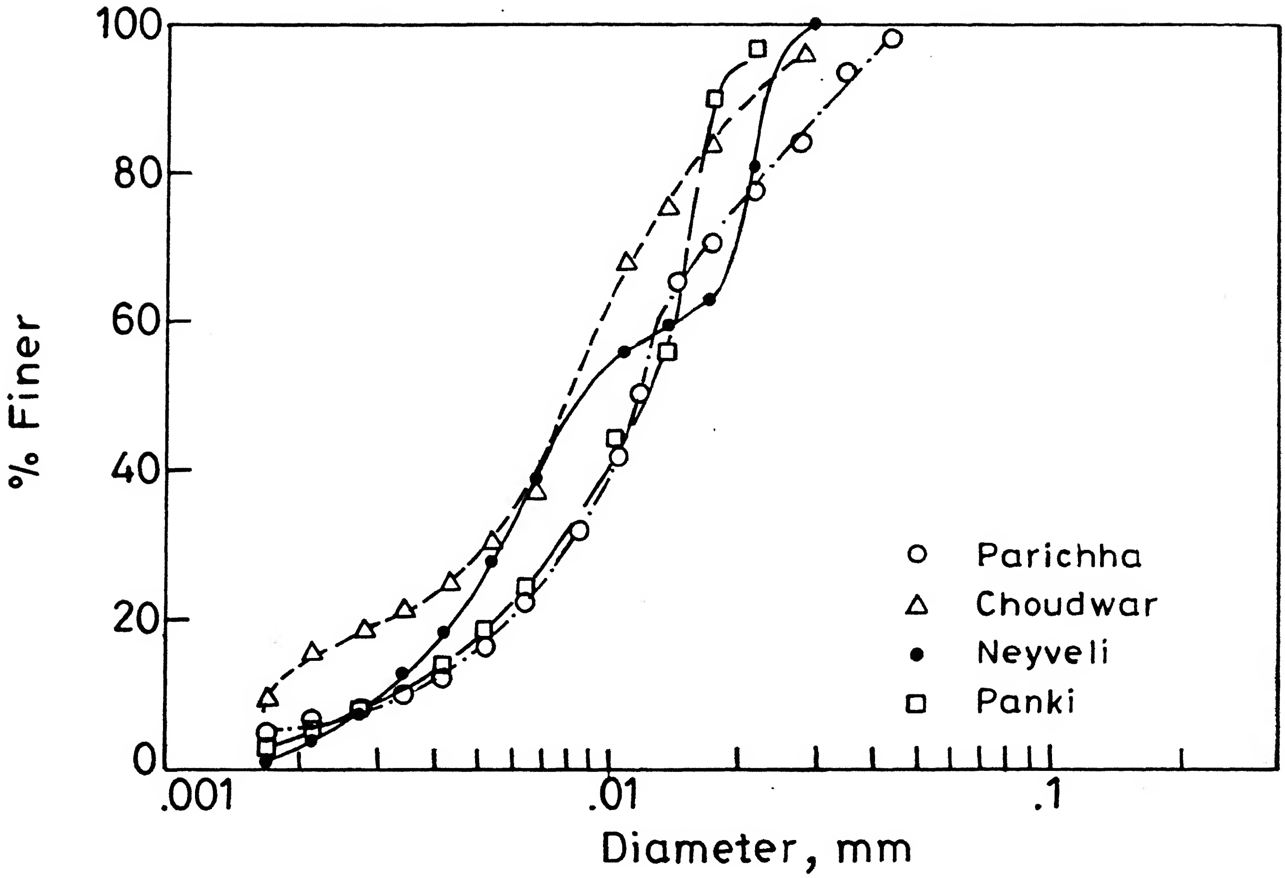


Fig-47 Particle size distribution using Coulter Counter method

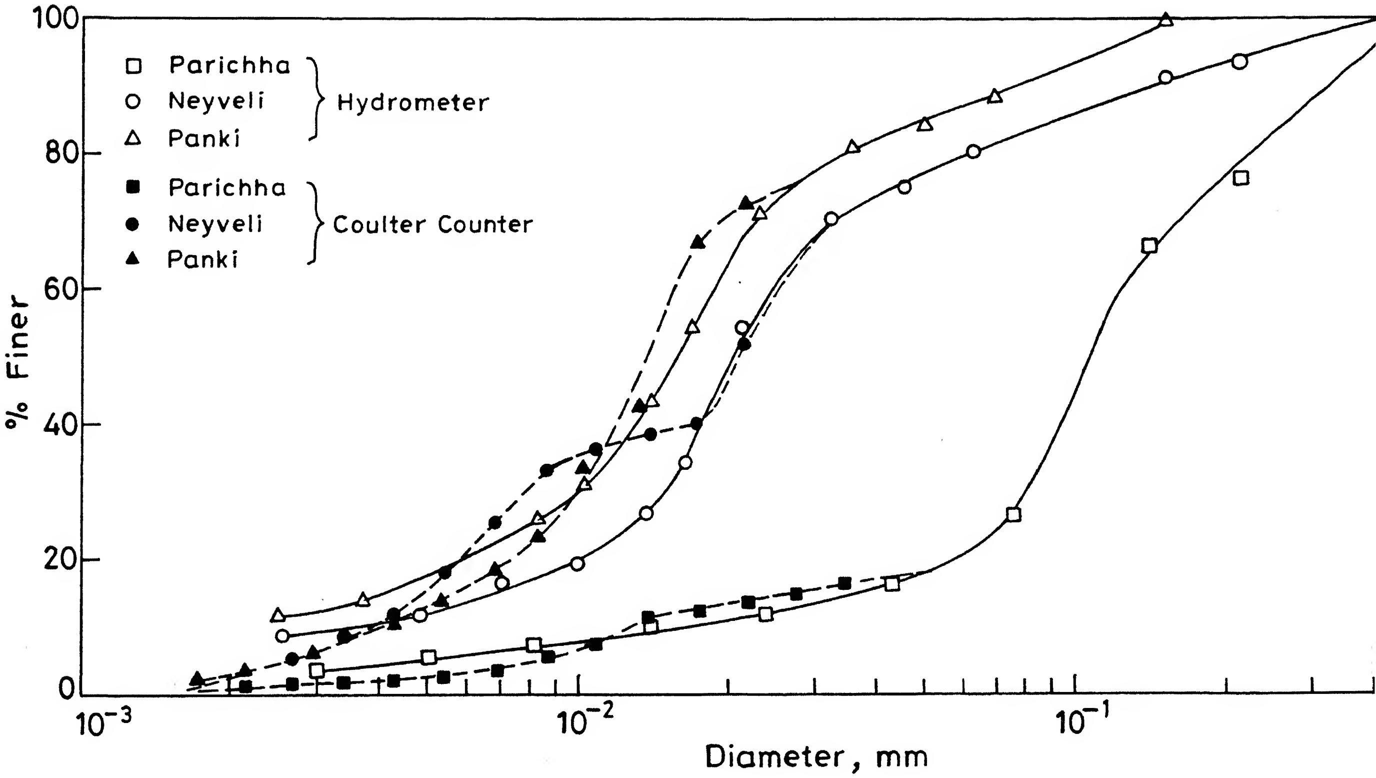


Fig-48 Comparision between Coulter counter and hydrometer results

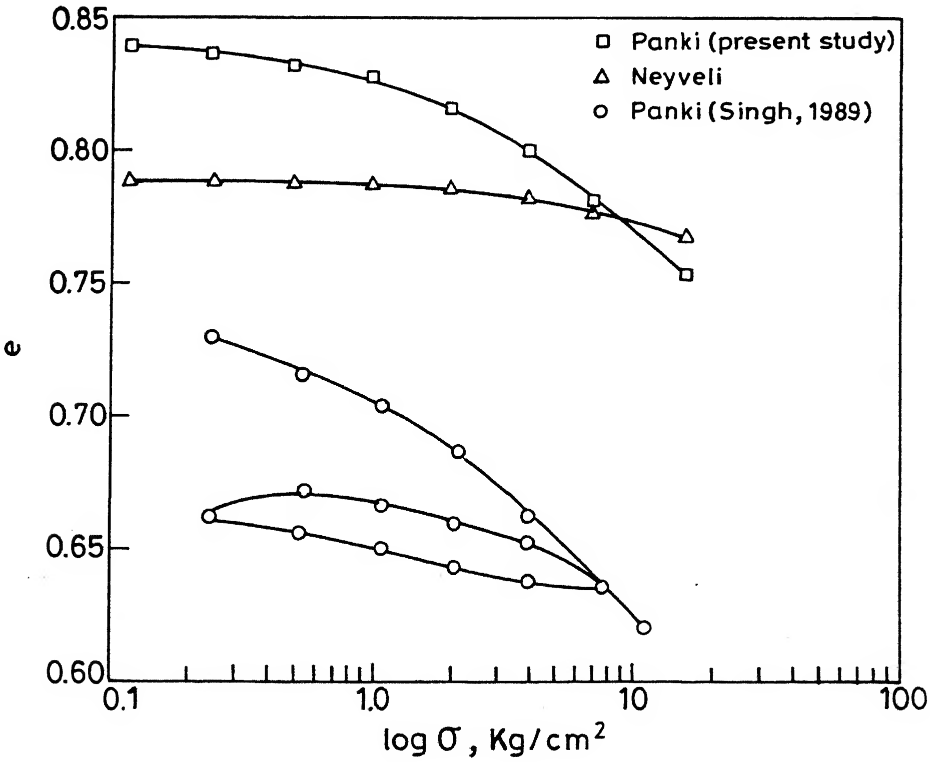


Fig-49 Compressibility of low calcium and high calcium fly ash

There is hardly any change in void ratio with stress. Obviously these fly ashes not poses any problems of settlement.

3.4.3 Compaction behavior

Fig-50 shows data for standard Harvard miniature compaction test for Panki and Neyveli, Panki-Neyveli and Neyveli-silt admixture and the local alluvial silt. The high calcium fly gives higher density and lower optimum moisture content compared to low calcium fly ash. This result is consistent with the general trend indicated in fig-51 and fig-52 (see Yudhbir and Honjo ;1991). In general fly ashes show considerable variability in compaction due to variation in the nature of fly ash produced from the same plant(fig-53). Results of Panki shown indicate similar trend. This has implication in terms of quality control specification of density and water content in the field compaction.

There are many factors like gradation, carbon content, iron content (see Singh;1989) etc. which control compaction characteristics of fly ashes, however, as reported by Yudhbir and Honjo(1991) γ_d is inversely and OMC is directly proportional to loss on ignition (carbon content) (fig-54). Results of present study are also indicated. It will be seen that for loss on ignition (carbon content) greater than 10 % there is a wide range of variation in value of OMC. However, in the modern plants one does not encounter such high value of carbon content in fly ash.

3.4.4 UNCONFINED COMPRESSION

Stress-strain behavior during unconfined compression test on samples cured for different duration and under different condition

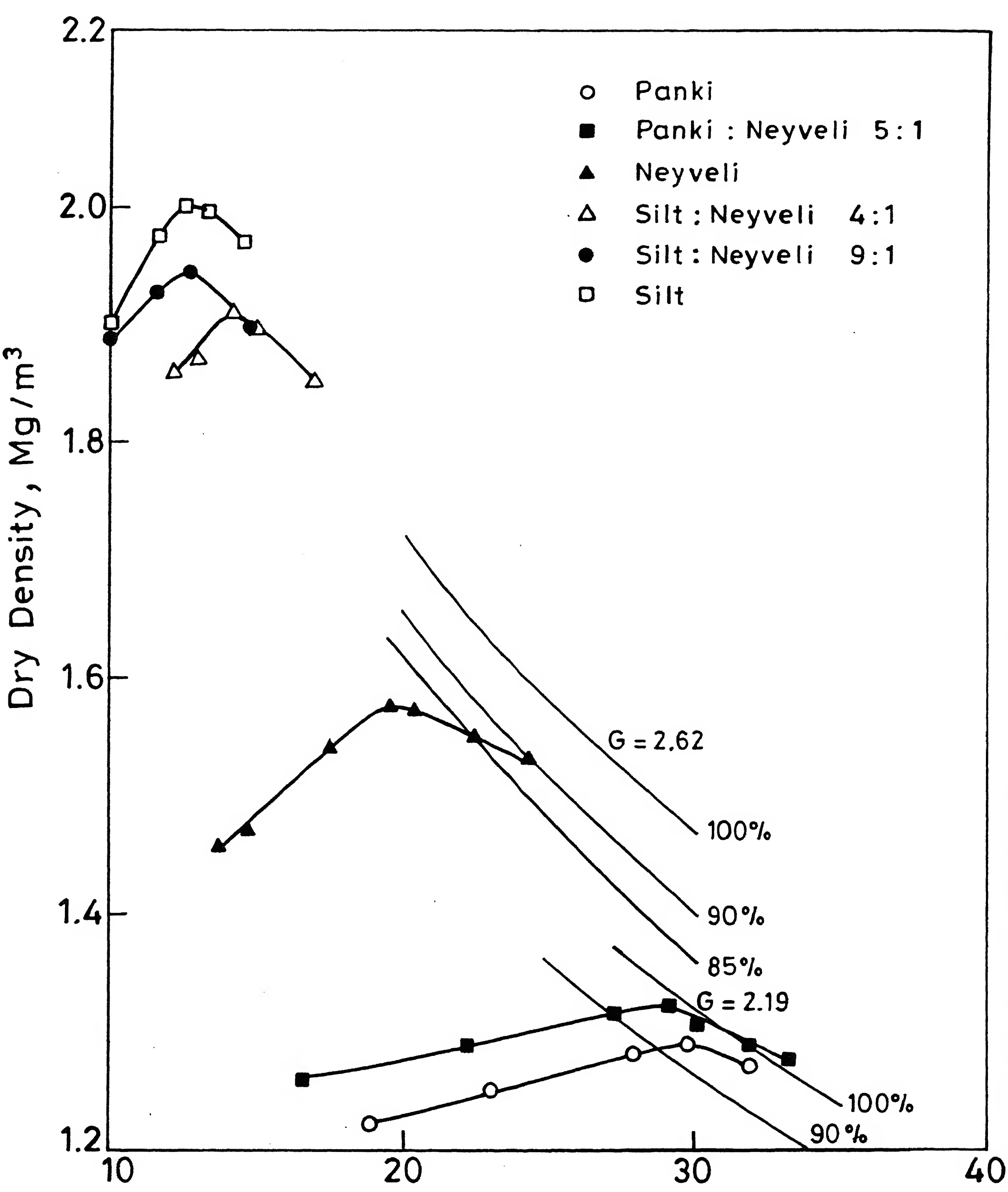


Fig-50 Compaction characteristics of fly ash tested

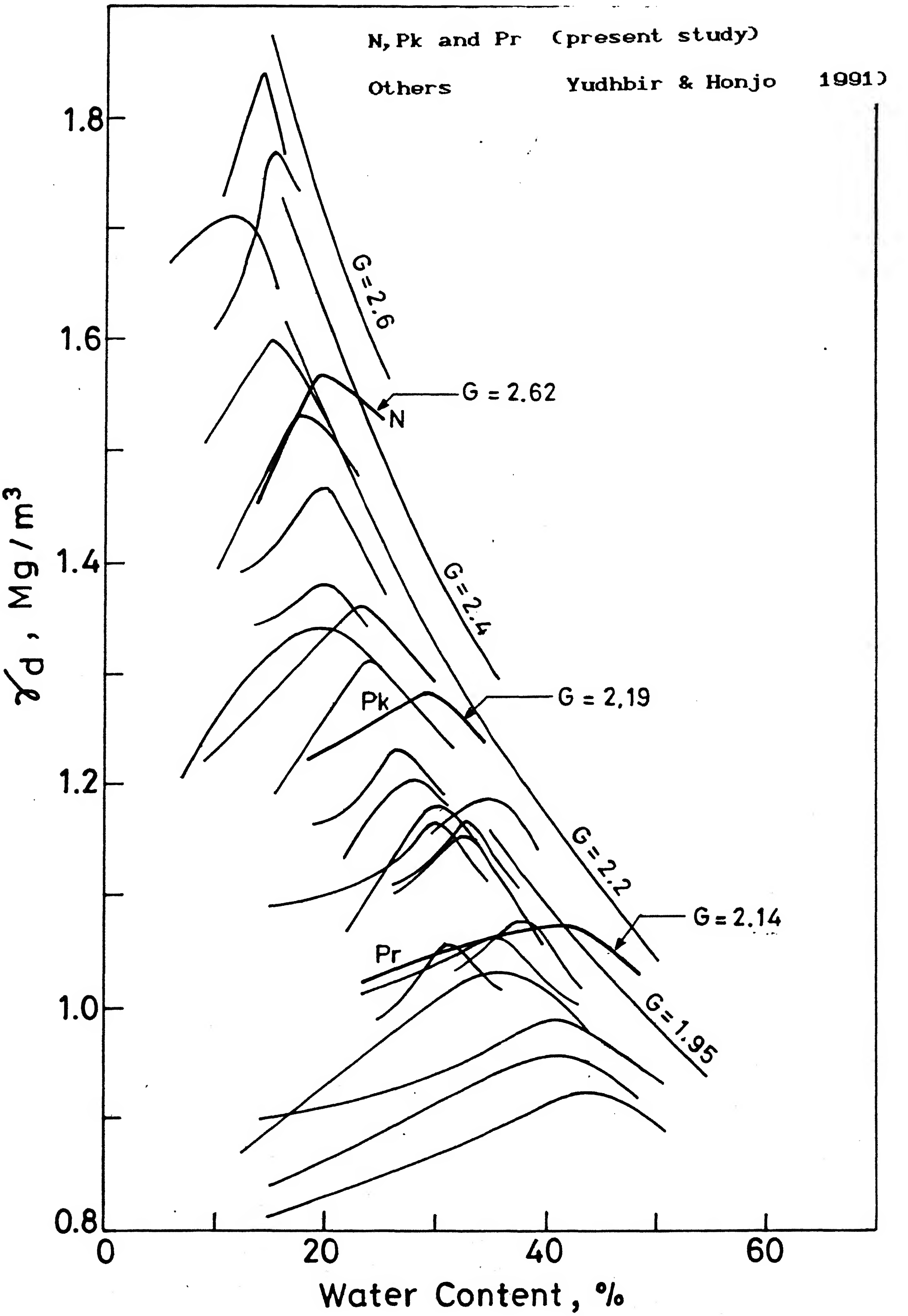


Fig-5.1 Comparision of compaction behavior of fly ashes

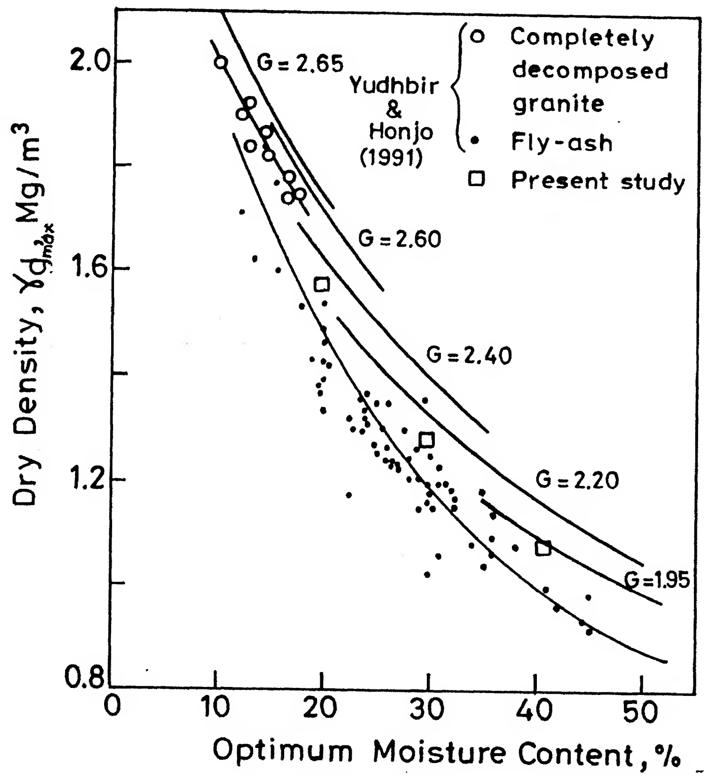


Fig-52 Relationship between γ_d max and OMC

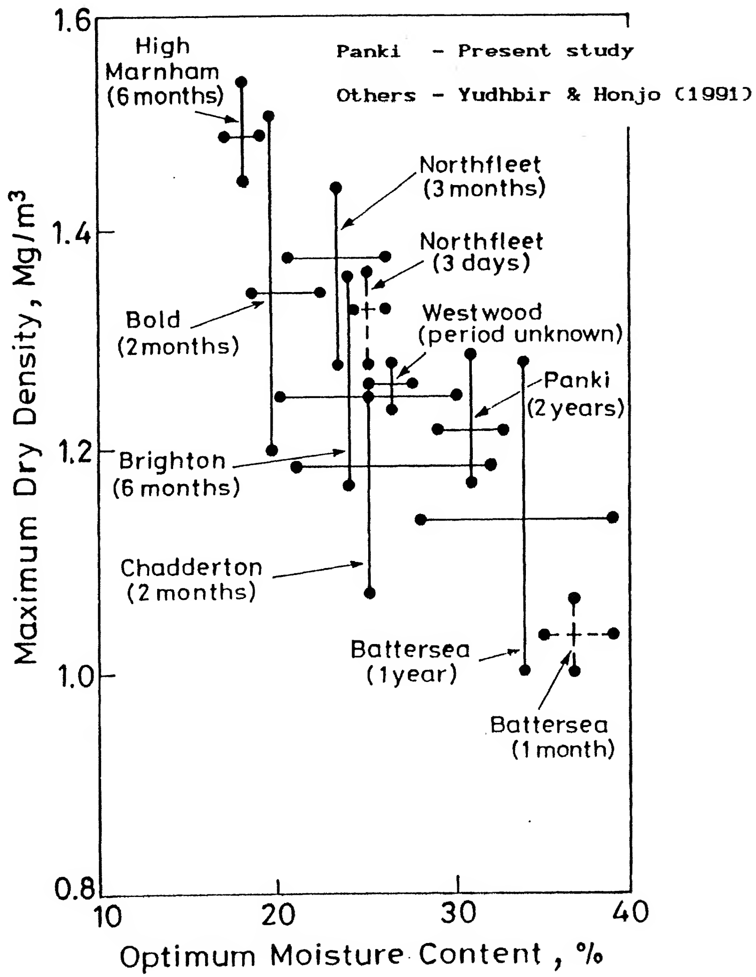
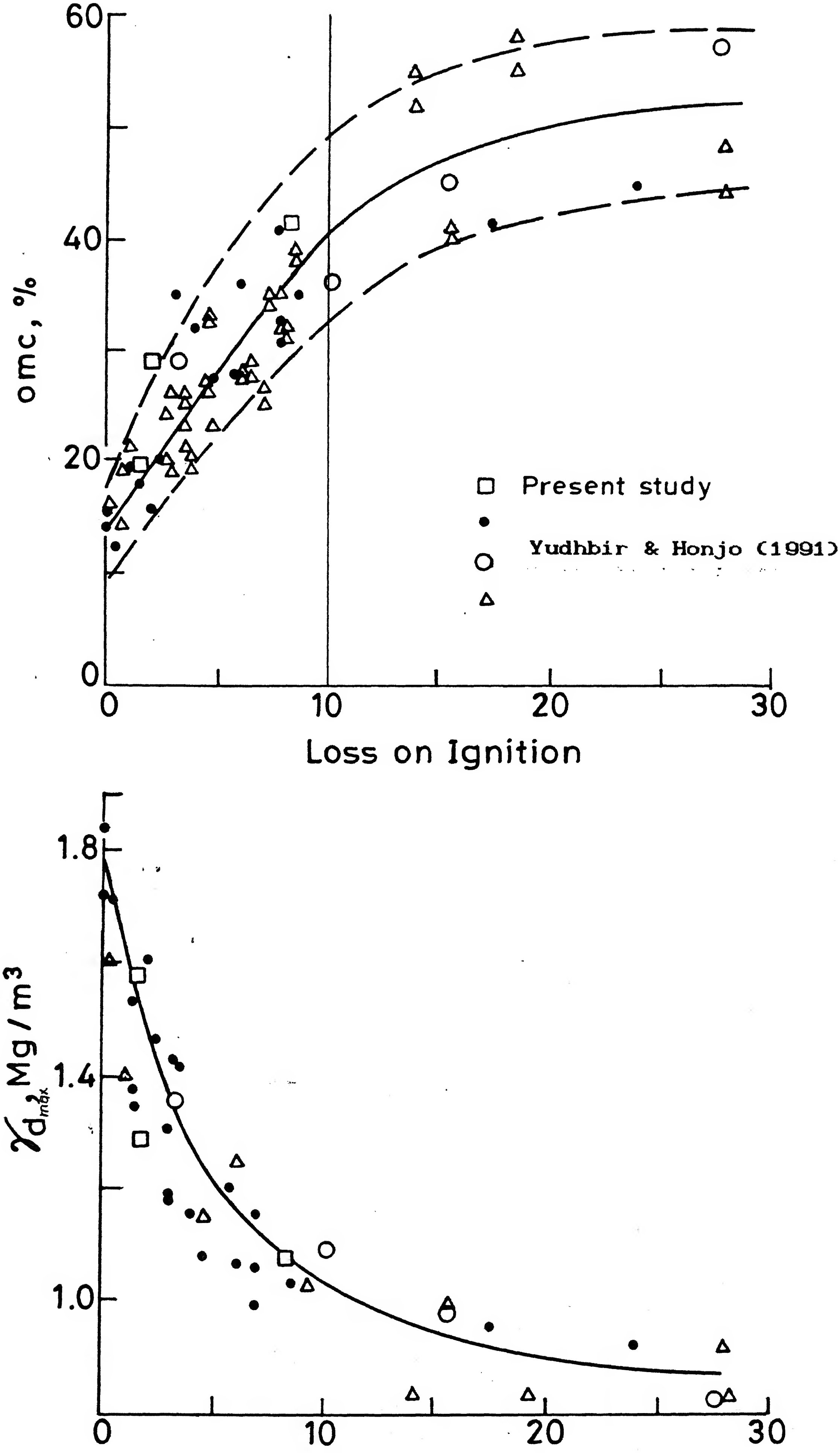


Fig-53 Variability in γ_d max and OMC over time



60
40
20
0
omc, %
0
10
20
30
Loss on Ignition
Present study
Yudhbir & Honjo (1991)
1.8
1.4
1.0
$\gamma_{d_{max}}$, Mg / m^3
0
10
20
30

for Parichha, Panki and Neyveli are given in fig-55, 56 and 57 respectively. Also shown are the relationship for as compacted samples of Parichha and Panki. It will be seen that the mode and duration of curing have significant influence on strength and stress-strain behavior. The post peak behavior especially for Panki and Neyveli is indicative of brittle rupture.

Relationship between failure strength and molding water content for low calcium and high calcium fly ashes are indicated in fig-58. It may be noted that in case of low calcium fly ashes, as compacted (at OMC) values of strength and water content shows a linear inverse relation ship. While curing in a desiccator with freely available water, strength increase (water content decreases) with time of curing. Curing out side in the open air, however, causes very large reduction in strength of low calcium fly ashes. This has a very important implication for using fly ash for construction of embankment. If compacted surface is left uncovered, the air drying would reduce strength very significantly resulting in degradation of the slope surface heading to surface erosion of loosened particles by both air and water.

This loss in strength in air drying supports the view put forth by DiGioia and Nuzzo(1972) that most of the ash compacted strength at OMC is due to capillary force only which are destroyed as the sample loss moisture in air drying. Rapid loss in strength and water content is due to large capillary size in the coarse Parichha fly ash as compared to Panki which is much finer. However, on wet curing the gain in strength in these fly ashes is due to self hardening

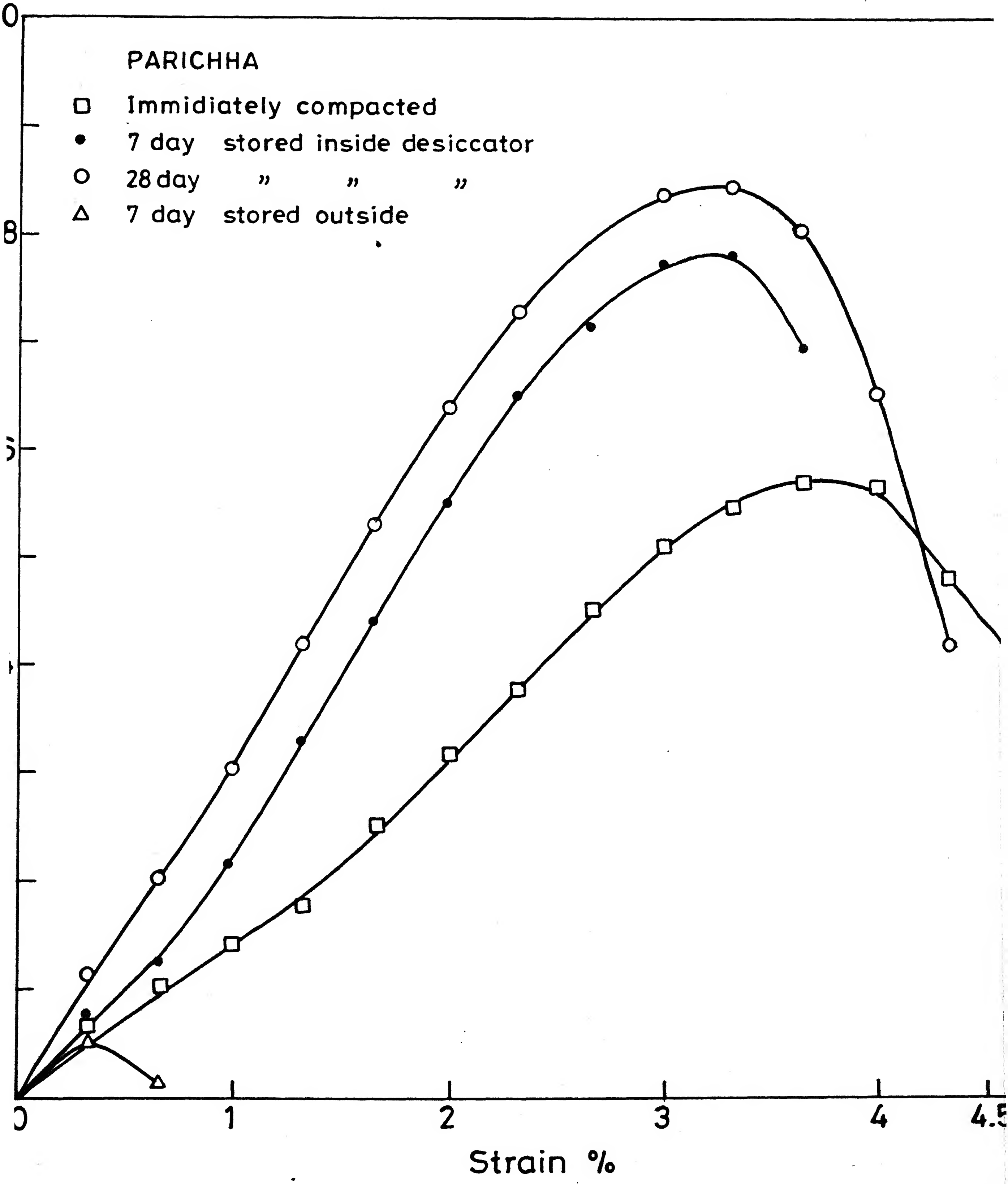


Fig-55 Unconfined compression test results for Parichha

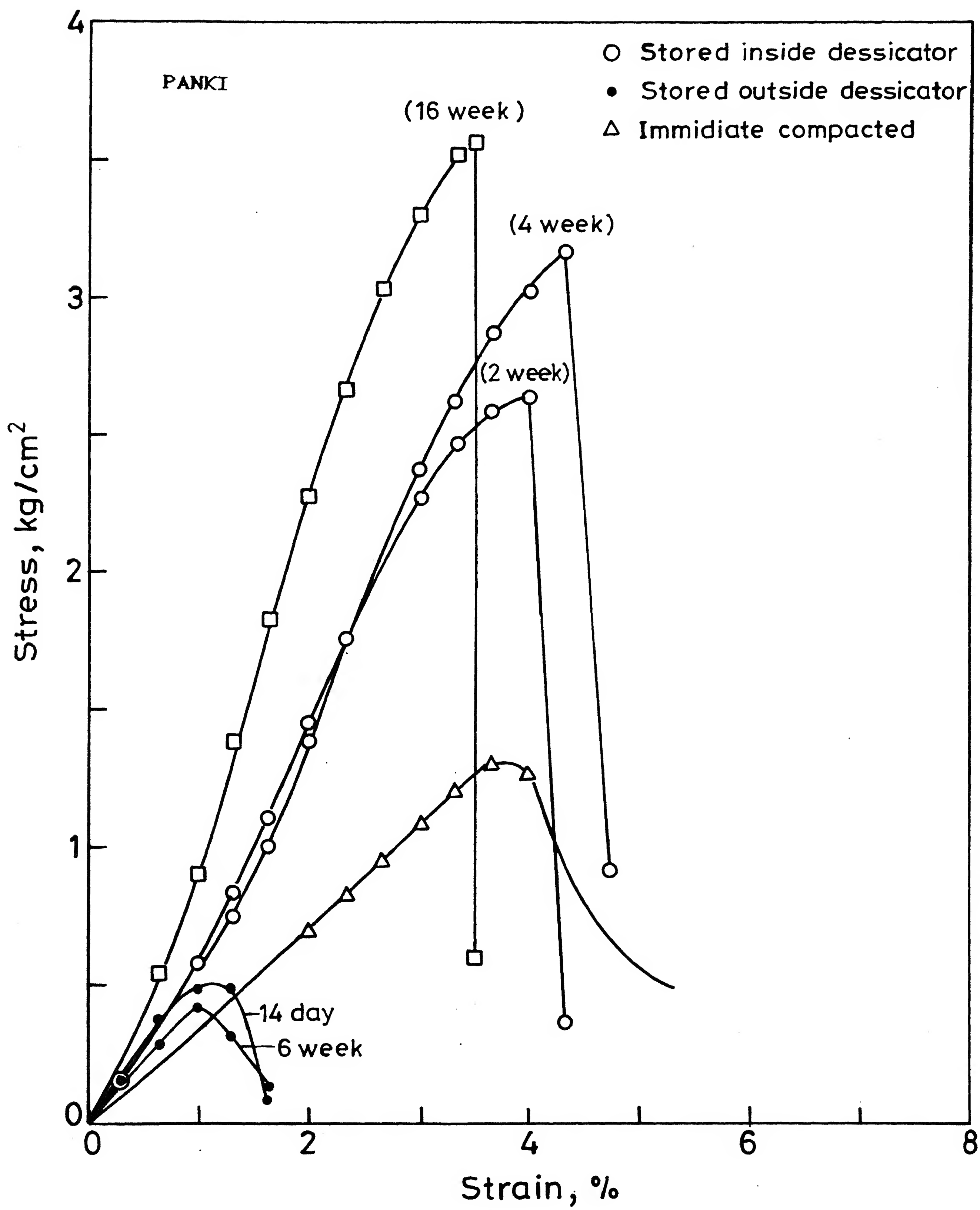


Fig-56 Unconfined compression test results for Panki

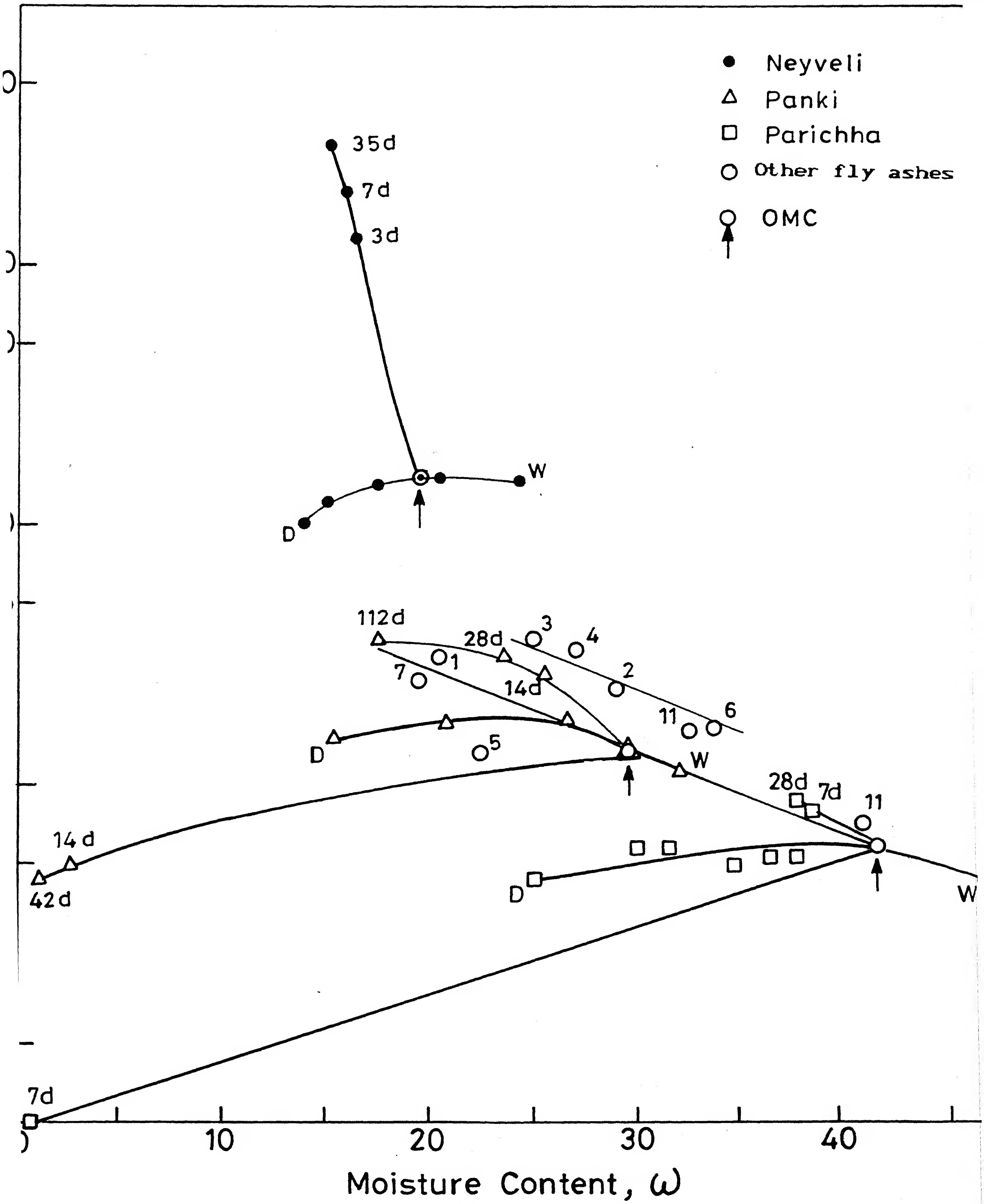


Fig-58 Unconfined strength vs molding water content with different

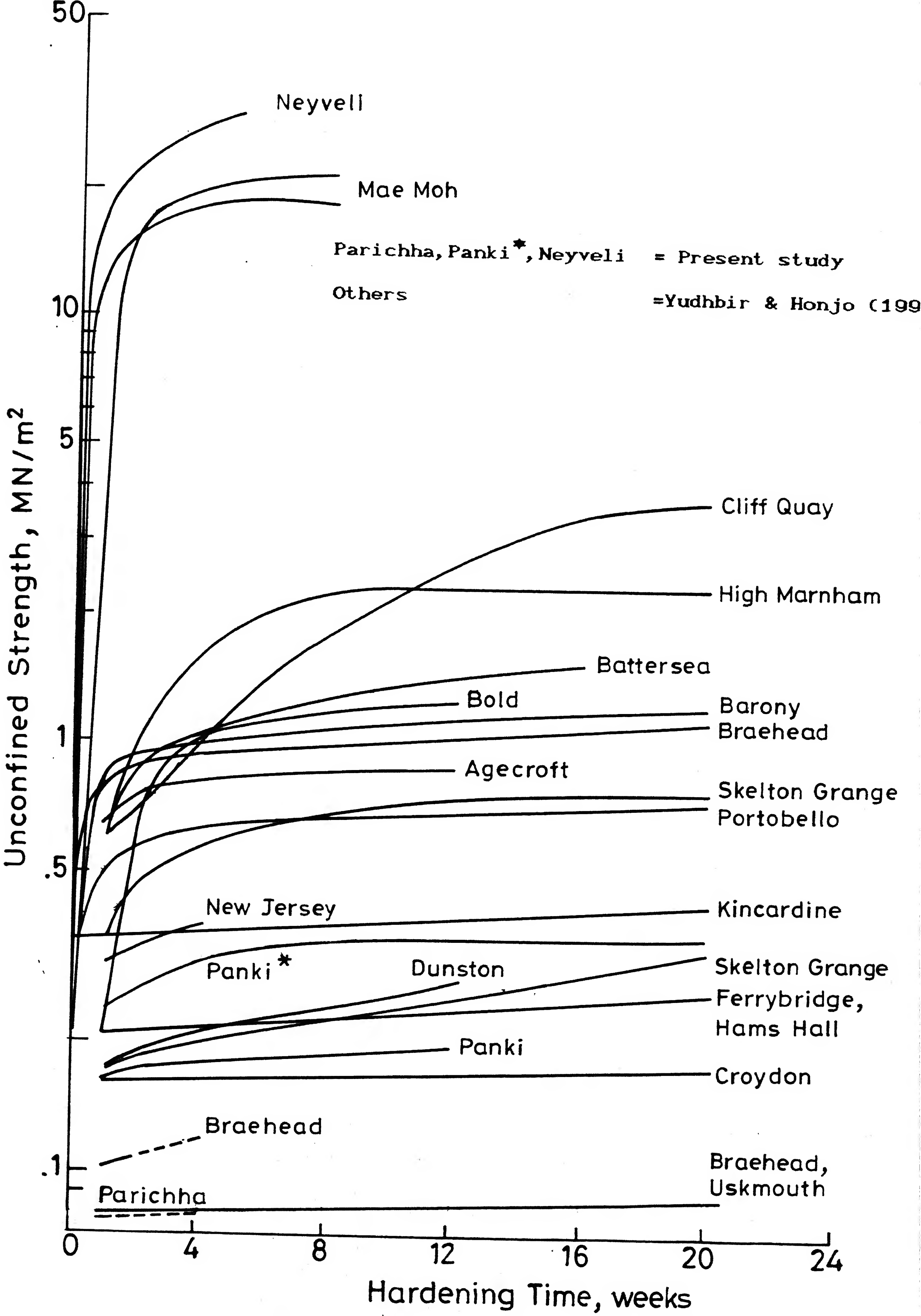
resulting from chemical reaction. As pointed out by Yudhbir and Honjo(1991), these fly ashes do not show significant self hardening due to lack of free lime and high calcium content.

The high calcium fly ash shows the strength-water relationship, for as compacted sample, similar to the low calcium fly ashes, however, the strength values are much higher which is attributed by Yudhbir and Honjo(1991) to high free lime and low or nil carbon content. Also the wet curing gives very large gain in strength and this is due to, as discussed in the next section, the presence of highly reactive minerals and glass content of these fly ashes.

3.4.5 GAIN IN STRENGTH WITH TIME

3.4.5.1 Self hardening

Yudhbir and Honjo(1991) pointed out that self hardening and pozzolanic reactivity of characteristics fly ashes are governed by different factors. They showed a relationship between free lime content and the 28 day strength samples compacted at OMC. The strength-time relation ship for majority fly ashes studied by them is reproduced in fig-59, where in data points from the present study are also given. It will be noted that there are clear three categories of fly ashes in respect of self hardening behavior. The high calcium fly ashes show very large gain in strength in about 4 weeks, where as the low calcium fly ashes can be subdivided into two groups —one giving higher initial gain up to 4 weeks and the other showing very slow increase in strength at a constant rate. Neyveli fits in the first category and Parichha and Panki belong to the third category.


Neyveli
Mae Moh
Parichha, Panki*, Neyveli = Present study
Others =Yudhbir & Honjo (199
Cliff Quay
High Marnham
Battersea
Bold
Barony
Braehead
Agecroft
Skelton Grange
Portobello
New Jersey
Kincardine
Panki*
Dunston
Skelton Grange
Ferrybridge,
Hams Hall
Panki
Croydon
Braehead
Braehead,
Uskmouth
Parichha
Unconfined Strength, MN/m²
Hardening Time, weeks
50
10
5
1
.5
.1
0
4
8
12
16
20
24

3.4.5.2 Pozzolanic reactivity

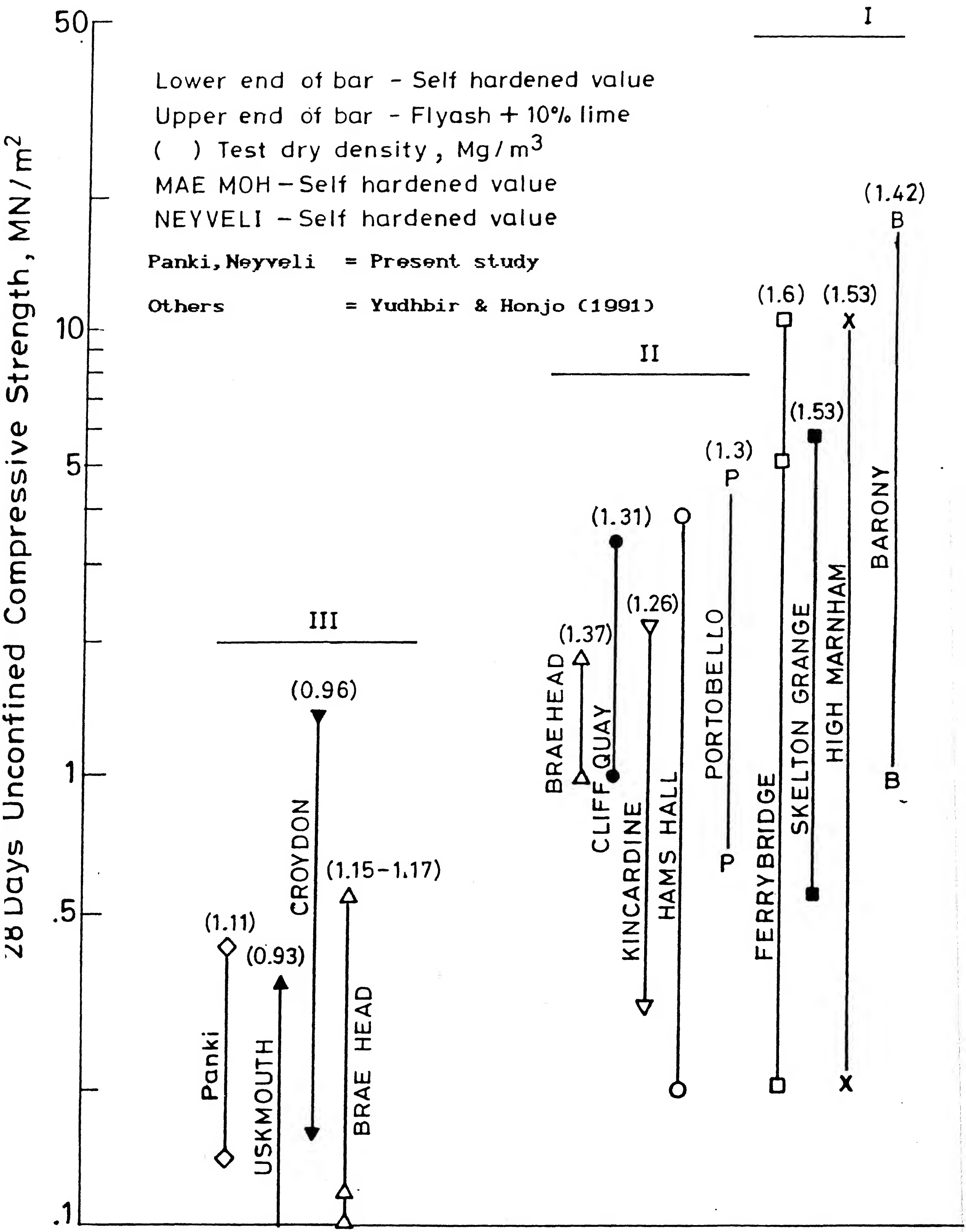
Gain in strength with addition of lime or cement indicates the pozzolanic reactivity of fly ash. Yudhbir and Honjo(1991) suggested classification of pozzolanic reactivity according to the three categories of fly ashes as indicated in fig-60.

Category I (considering low calcium fly ashes only) is represented by a 28 day strength of compacted sample at OMC with 10 % lime, in the range 10 Mn/m^2 or higher, category II represents 28 day strength in range of 2-10 Mn/m^2 where as category III fly ashes show 28 day strength less than 2 MN/m^2. Panki fly ash once again lies in the category III.

It may be noted that every fly ash with poor self hardening behavior is not necessarily characterized by poor pozzolanic reactivity. Pozzolanic reactive depends on the quality and quantity of glass content, the carbon and the fineness of the fly ash. This is well brought out by fly ashes like Ferry bridge, Skelton grange etc which represented category III in fig-59 and fall in category I in fig-60.

3.5 APPLICATION

Fly ash, specially low calcium fly ashes, can be utilized as geotechnical construction materials for embankment and reclamation fills. Yudhbir and Honjo(1991) have reviewed their uses and have shown that these materials are ideal for substitute for granular fills. The good low calcium fly ash may either be used without any additives (in case it exhibits higher self hardening behavior) or be mixed with lime or cement (the amount of additives depending upon



28 Days Unconfined Compressive Strength, MN/m2
50
10
5
1
.5
.1
Lower end of bar - Self hardened value
Upper end of bar - Flyash + 10% lime
( ) Test dry density, Mg/m3
MAE MOH - Self hardened value
NEYVELI - Self hardened value
Panki, Neyveli = Present study
Others = Yudhbir & Honjo (1991)
I
II
III
(1.42)
B
BARONY
B
(1.6)
(1.53)
X
HIGH MARNHAM
X
(1.53)
SKELTON GRANGE
FERRYBRIDGE
(1.3)
P
PORTOBELLO
P
HAMS HALL
(1.26)
KINCARDINE
(1.31)
CLIFF QUAY
(1.37)
BRAEHEAD
(0.96)
CROYDON
(1.15-1.17)
BRAE HEAD
(1.11)
Panki
(0.93)
USKMOUTH

quality and quantity of glass present and the carbon content) to obtain increase in strength of constructed embankments. The poor low calcium fly ashes would have to be mixed with chemical additives like $CaCl_2$, $CaSO_4$ etc. to enhance the reactivity of fly ash with lime or cement.

The high calcium fly ashes (CaO > 15-20%) like Neyveli obviously are to be used either in mortar (as in case for this fly ash) with cement or in the preparation of mass concrete as replacement of cement. Such a fly ash may also be used to make relatively light weight aggregate or for making fly ash-cement blocks etc. .

In geotechnical engineering, such a fly ash is an excellent additive to improve engineering properties of soils. Limited tests on mixture of local alluvial silt with 10-20% of Neyveli fly ash showed considerable improvement in CBR and unconfined strength values. In fact the CBR value of a compacted silty clay with 10% Neyveli admixture gave such a high improvement in bearing resistance that it was not possible to test for CBR in set up normally used for testing of soils. Koo(1991) reports as high as 300% CBR value for compacted high calcium fly ash (similar to Neyveli) after 20 days. Alluvial silty clay compacted at OMC with 20% Neyveli admixture gave unconfined strength value of about 40 Kg/cm^2 after 7 days of curing as compared to a 2 Kg/cm^2 value of untreated as compacted clay at OMC.

Neyveli fly ash when added to low calcium fly like Panki showed significant improvement in the unconfined strength of the compacted amples. The unconfined compressive strength value of Panki fly ash

as compacted at OMC was of the order 1.3 Kg/cm^2 which increased to 10 Kg/cm^2 after 3 days of curing when the Panki fly ash was mixed with 20% of Neyveli fly ash and compacted at OMC. These limited test results suggest that high calcium fly ashes can be used for improvement of soil and low calcium fly ashes and this is likely to be more cost effective way of improvement of soil or low calcium fly ashes for geotechnical construction as compared to the use of lime or cement as additives.

As pointed out earlier , the surface of embankment of untreated compacted low calcium fly ashes need to be protected so as to prevent air drying and loss of strength. A surface coating of either treated fly ash or clayey soil would be necessary to ensure that compacted fly at least retains its as compacted strength.

CHAPTER IV

CONCLUSION AND RECOMMENDATION

4.1 Conclusion

Based on the findings of investigations reported here the following main conclusion may be arrived at:

1. SEM provides a best tool to study the morphological characteristics of different fly ashes.

2. The broad morphological forms of fly ashes as reported by Watt and Thorne(1965) using optical microscope were generally presented in the fly ashes investigated.The SEM studies, however, helps to reveal the surface characteristics in much more detail. The existence of tiny surface coatings and swiss cheese like morphological patterns of carbon(fig-11) Diamond(1983), Fischer and Natusch(1979) be identified with help of SEM.

3. Iron rich particles have been shown to posses a characteristic cubic pattern iron spinel structure-in case of high calcium with high iron content

4. Low calcium fly ash spherical particles are covered with large numbers of small to relatively large surface droplets resulting from condensation and solidification of inorganic substance rich in Si and Al (fig-7). The high calcium fly ashes on the contrary shows spherical particles with extensive calcium coatings (fig-9). In case of high calcium fly ash, two layers of glass phase comprising a particle have been detected (fig-15(b) & 17). A typical needle-frame work structure of mullite crystals present in low calcium fly ashes is revealed after treated with HF acid (fig-14(b)).

5. Clustered particles in both low and high calcium fly ashes are identified (fig-12(a) & (b)). Mechanism of clustering proposed by Diamond(1986) are shown to be appropriate. It is suggested that for high carbon, low calcium fly ashes, a thin layer of carbon acts as binder whereas in other cases fused glass contacts are likely to be cause of producing clustered particles.

6. EDX is shown to be the best method to study elemental composition of different grains comprising a fly ash. Though this method is semi-quantitative but it has the advantage of giving variation in chemical as opposed to average values of chemical composition are reported.

7. The low calcium fly ashes are shown to be rich in Si and Al and heir floaters indicate higher values of K compared to that present in he whole fly ash. Also the chemical composition of different fraction s essentially similar, which is consistent with the findings of ischer and Natusch(1979).

8. The high calcium fly ashes are rich in Ca and Al and their finer raction have higher proportion of Mg and S compared to the whole fly sh. Unlike low calcium fly ashes, these exhibit different chemical omposition for coarse and finer fraction, the former being rich in Si id Fe and the latter are in Ca, Al, S, and Mg. The coarser fraction are ss reactive compared to the finer fraction. Presence of free lime quires that floaters be collected from say methanol rather than ter suspension. The particles of this fly ash consist of two layers, e inner one is rich in Al and Si and the outer layer is rich in Ca d Al.

9. The minerals in low calcium fly ashes are quartz, mullite,

hematite, and magnetite which are inert. The mineralogy of low calcium fly ashes does not vary with particle size.

10. The Neyveli high calcium fly ash contains highly reactive minerals like C_3A, CS, $C\bar{S}$ along with quartz, hematite and magnetite. The hydration of these reactive minerals form minerals like ettringite which are responsible for gain in strength with time.

11. Based on the XRD pattern and location of *hump* the quality of glass phase can be found out. A relationship between the analytical lime content and *hump* position(2θ) is shown (fig-45) to be a good indicator for study of type of glass as suggested by Diamond(1983). For CaO < 1% the predominant glass type is siliceous ($2\theta=21^{o}-22^{o}$) and for CaO up to 15-20% alumino-silicate variety glass is indicated by $2\theta=26^{o}-27^{o}$. In between these ranges of CaO content siliceous and alumino-silicate glass admixture are indicative.

For CaO ≥ 20% a sudden transition from alumino-silicate to calcium-aluminate glass is observed. Calcium-aluminate glass is indicated by $2\theta = 32^{o}$.

12. The quantity of glass can be predicted from the K/A vs. glass content relationship which was initially suggested by Hubbard et al (1985). The data on high K content of glassy floater presented here further validates this relationship.

13. The residual carbon content(LOI) seems to be the controlling factor for compaction characteristic of fly ash though the factors like iron content, gradation, morphology etc. also affect this compaction characteristics.

14. Most of the compressive strength of as compacted samples at OMC is due to capillary forces which are destroyed as the sample is air

dried. The gain in strength with time (self hardening) results from chemical reactivity due to the presence of free lime as illustrated by Yudhbir and Honjo(1991). The gain in strength with time with addition of lime or cement termed as pozzolanic reactivity depends upon factors such as quality and quantity of glass, carbon content, fineness etc..

4.2 Recommendation

Based on these conclusions, the following recommendations are made regarding behavior of fly ashes and their use potential.

1. Proportion of particles >75μm is a good index of reactive potential of high calcium fly ashes and as such it may be useful to quote the proportion of coarse fraction for these fly ashes. In case of low calcium fly ashes however, gradation has practically no important bearing on the behavior of a given fly ash.
2. Particle size distribution for high calcium fly ashes should be conducted by method such as Coulter counter and not by the hydrometer procedure.
3. In case of low calcium fly ashes used for construction of embankments, the surface must be protected against drying due to evaporation.
4. Distinction should be made between self hardening and pozzolanic potential especially of low calcium fly ash. While the former is controlled by the free lime and carbon content, the latter is governed by the quality and quantity of glass, the carbon content and possibly the fineness.
5. Before recommending use of a fly ash either as a good geotechnical construction material or as a replacement of cement, it

is important to characterize fly ash in terms of morphology, chemistry and mineralogy through the use of SEM, EDX, and XRD techniques. This quantitative characteristics will help in economic and effective utilization of fly ash. This recommendation emphasizes an important fact that fly ashes are highly variable material and no two fly ashes are expected to be similar.

Following points may be recommended for further work in this direction:

It will be very useful to try to establish a quantitative index reflecting the effect of chemistry and mineralogy of both crystalline and amorphous phase of fly ash on its pozzolanic reactive potential.

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APPENDIX - 1

Source	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	C	TiO_2	MISC $MgO+Na_2O+K_2O$
Spain	46.9	23.5	7.8	10.6	0.5	1.4	-	-
	49.2	29.6	4.2	2.8	0.9	5.9	-	-
	50.8	32.1	4.7	1.9	1.0	4.5	-	-
	51.2	30.8	6.4	3.0	0.4	5.7	-	-
	45.7	26.9	8.8	9.9	1.4	4.3	-	-
	49.3	27.9	6.5	4.5	0.6	5.3	-	-
	51.3	31.1	5.9	3.2	0.7	5.2	-	-
	45.0	36.8	7.4	4.4	1.4	2.9	-	-
	45.4	30.0	16.1	4.0	1.9	0.8	-	-
	40.1	20.6	12.6	21.1	3.7	0.3	-	-
USA	58.6	21.3	3.3	11.1	0.3	0.77	-	-
	53.7	23.2	3.86	12.5	0.3	0.49	-	-
	52.0	21.2	5.08	10.5	0.5	0.10	-	-
	48.8	21.5	10.6	5.95	1.0	6.30	-	-
	43.7	22.7	15.7	3.82	1.7	7.34	-	-
	45.5	22.5	20.1	1.29	1.0	2.53	-	-
	37.1	12.3	38.9	4.45	1.8	0.42	-	-

43.2	22.1	3.45	13.0	0.9	0.53	-	-
41.2	21.1	3.92	12.4	6.8	0.15	-	-
47.2	19.5	18.2	5.3	-	0.43	-	-
47.4	34.0	9.0	2.3	-	3.17	-	-
38.2	25.7	16.3	3.9	-	11.13	-	-
44.9	34.0	6.5	2.3	-	7.22	-	-
36.80	18.1	6.21	27.83	1.9	0.55	4.74	
35.20	26.0	7.95	3.57	0.6	2.22	0.97	
34.10	16.05	6.30	26.49	2.9	0.2	6.32	1.39
51.70	19.96	6.43	16.57	1.51	0.3	3.91	0.59
30.64	17.27	4.93	27.80	2.65	0.2	6.47	2.88
33.06	20.08	5.41	24.72	1.47	0.2	4.94	2.93
50.62	26.87	10.9	2.05	0.41	1.27	4.60	-
55.10	21.10	5.2	6.7	0.5	-	-	1.6+1.73+1.24
55.4	22.0	6.3	6.8	0.5	-	-	2.0+2.86+0.67
50.9	25.3	8.4	2.4	0.3	-	-	1.0+0.28+2.83
57.6	29.0	5.2	0.3	0.2	-	-	1.1+0.3+2.9
52.2	27.4	9.2	4.4	0.45	-	-	1.0+0.12+0.68
50.9	28.9	5.4	1.4	0.40	-	-	0.9+0.32+2.54

	46.2	31.3	8.5	1.8	0.5	-	-	0.7+0.25+1.99
	38.4	13.0	20.6	14.6	3.3	-	-	1.4+0.4+2.04
	39.5	19.5	5.7	24.7	1.8	-	-	3.42+1.56+0.2
	36.0	19.8	5.0	27.2	3.15	-	-	4.92+0.42+172
	50.5	17.2	5.9	15.8	2.7	-	-	3.1+0.49+0.8
	55.6	22.7	4.3	13.3	0.16	-		- -
U.K.	45.8	27.1	7.4	1.9	0.3	1.0	-	1.7+1.5+2.8
	47.4	25.8	8.7	3.9	0.4	1.1	-	1.8+2.0+2.6
	44.9	26.5	11.4	3.0	0.4	1.0	-	1.9+1.1+2.2
	50.6	29.2	9.0	2.5	0.4	1.1	-	2.0+1.2+1.9
	48.8	28.4	9.1	2.8	0.4	1.10	-	2.2+1.7+1.8
	51.8	24.2	10.4	2.4	0.3	1.0	-	1.9+2.1+2.7
	49.0	26.9	9.7	5.5	0.3	1.1	-	2.1+1.3+2.2
	48.7	29.6	11.1	3.5	0.4	1.0	-	1.6+1.2+2.1
	49.1	26.4	8.9	2.3	0.3	1.1	-	1.9+2.2+2.8
	43.4	21.1	8.5	7.4	1.0	0.8	-	1.9+4.9+1.9
	46.8	24.9	10.1	7.6	0.5	1.0	-	1.9+2.7+1.8
	50.4	26.1	10.1	7.9	0.54	1.0	-	1.7+1.7+2.8

	48.2	27.5	9.6	3.0	0.40	1.0	-	2.1+1.0+3.
	48.6	28.6	10.1	3.0	0.3	1.1	-	2.2+0.8+2.
	49.3	26.7	11.0	1.6	0.2	1.0	-	2.0+1.3+3.
	50.1	27.6	10.3	1.4	0.4	1.0	-	2.1+1.5+3.
	47.7	27.0	9.9	1.2	0.5	1.1	-	2.0+1.7+2.
	50.6	24.7	9.5	2.0	0.5	1.0	-	2.1+4.0+3.
	47.9	34.1	5.8	2.8	0.2	1.3	-	1.6+0.4+1.
	47.4	32.3	5.8	3.8	0.1	1.4	-	1.2+0.3+1.3
	52.2	32.2	5.8	2.4	0.2	1.1	-	1.9+0.4+2.4
	50.2	27.4	10.3	1.4	0.3	1.0	-	1.9+1.3+3.0
	47.6	27.1	10.2	3.6	0.4	0.9	-	2.1+0.9+3.0
	47.3	30.3	10.3	3.1	0.3	1.1	-	1.7+1.3+2.4
	48.0	34.4	7.1	3.2	0.2	1.5	-	1.7+0.1+1.3
	51.2	26.3	10.3	1.6	0.4	1.0	-	1.8+1.8+2.8
Panki	65.1	26.0	4.5	2.4	0.27	1.70	0.47	0.35+- + -
Neyveli	26.4	25.4	25.7	16.6	1.00	2.45	0.55	0.85+ - + -